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# THE ELECTRON



ROBERT ANDREWS MILLIKAN

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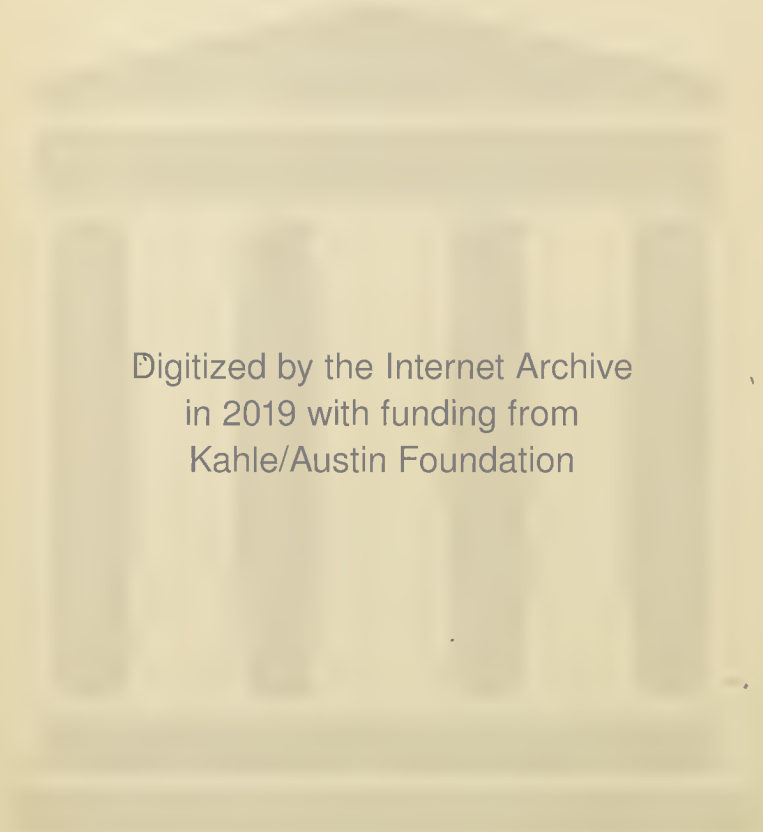
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John S. Barnes  
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## THE ELECTRON

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# THE ELECTRON

ITS ISOLATION AND MEASUREMENT AND THE  
DETERMINATION OF SOME OF  
ITS PROPERTIES

*By*

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TO  
ALBERT A. MICHELSON  
AND  
MARTIN A. RYERSON  
THIS SMALL OUTGROWTH OF THEIR  
INSPIRATION AND GENEROSITY  
IS RESPECTFULLY DEDICATED

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## PREFACE

It is hoped that this volume may be of some interest both to the physicist and to the reader of somewhat less technical training. It has been thought desirable for the sake of both classes of readers, not to break the thread of the discussion in the body of the book with the detailed analyses which the careful student demands. It is for this reason that all mathematical proofs have been thrown into appendixes. If, in spite of this, the general student finds certain chapters, such as vii and viii, unintelligible, it is hoped that without them he may yet gain some idea of certain phases at least of the progress of modern physics.

R. A. MILLIKAN

May 18, 1917



## PREFACE TO THE SECOND EDITION

In the present edition of this book I have endeavored to present a simple treatment of all the developments in physics to date which have caused a modification or extension of any of the viewpoints expressed just seven years ago. In its preparation I have been very much impressed to find how uniformly the changes represent additions rather than subtractions—a striking illustration of the great truth that science, like a plant, grows in the main by the process of accretion. If I have succeeded in interesting some old friends and making a few new ones for one of the most fascinating of subjects, I shall be content.

ROBERT ANDREWS MILLIKAN

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PASADENA, CALIFORNIA  
May 18, 1924



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## INTRODUCTION

Perhaps it is merely a coincidence that the man who first noticed that the rubbing of amber would induce in it a new and remarkable state now known as the state of *electrification* was also the man who first gave expression to the conviction that there must be some great unifying principle which links together all phenomena and is capable of making them rationally intelligible; that behind all the apparent variety and change of things there is some primordial element, out of which all things are made and the search for which must be the ultimate aim of all natural science. Yet if this be merely a coincidence, at any rate to Thales of Miletus must belong a double honor. For he first correctly conceived and correctly stated, as far back as 600 B.C., the spirit which has actually guided the development of physics in all ages, and he also first described, though in a crude and imperfect way, the very phenomenon the study of which has already linked together several of the erstwhile isolated departments of physics, such as radiant heat, light, magnetism, and electricity, and has very recently brought us nearer to the primordial element than we have ever been before.

Whether this perpetual effort to reduce the complexities of the world to simpler terms, and to build up the infinite variety of objects which present themselves to our senses out of different arrangements or motions of the least possible number of elementary substances, is a

modern heritage from Greek thought, or whether it is a native instinct of the human mind may be left for the philosopher and the historian to determine. Certain it is, however, that the greatest of the Greeks aimed at nothing less than the complete banishment of caprice from nature and the ultimate reduction of all her processes to a rationally intelligible and unified system. And certain it is also that the periods of greatest progress in the history of physics have been the periods in which this effort has been most active and most successful.

Thus the first half of the nineteenth century is unquestionably a period of extraordinary fruitfulness. It is at the same time a period in which for the first time men, under Dalton's lead, began to get direct, experimental, quantitative proof that the atomic world which the Greeks had bequeathed to us, the world of Leucippus and Democritus and Lucretius, consisting as it did of an infinite number and variety of atoms, was far more complex than it needed to be, and that by introducing the idea of molecules built up out of different combinations and groupings of atoms the number of necessary elements could be reduced to but about seventy. The importance of this step is borne witness to by the fact that out of it sprang in a very few years the whole science of modern chemistry.

And now this twentieth century, though but twenty-four years old, has already attempted to take a still bigger and more significant step. By superposing upon the molecular and the atomic worlds of the nineteenth century a third electronic world, it has sought to reduce the number of primordial elements to not more than two, namely, positive and negative electrical charges. Along

with this effort has come the present period of most extraordinary development and fertility—a period in which new viewpoints and indeed wholly new phenomena follow one another so rapidly across the stage of physics that the actors themselves scarcely know what is happening—a period too in which the commercial and industrial world is adopting and adapting to its own uses with a rapidity hitherto altogether unparalleled the latest products of the laboratory of the physicist and the chemist. As a consequence, the results of yesterday's researches, designed for no other purpose than to add a little more to our knowledge of the ultimate structure of matter, are today seized upon by the practical business world and made to multiply tenfold the effectiveness of the telephone or to extract six times as much light as was formerly obtained from a given amount of electric power.

It is then not merely a matter of academic interest that electricity has been proved to be atomic or granular in structure, that the elementary electrical charge has been isolated and accurately measured, and that it has been found to enter as a constituent into the making of all the seventy-odd atoms of chemistry. These are indeed matters of fundamental and absorbing interest to the man who is seeking to unveil nature's inmost secrets, but they are also events which are pregnant with meaning for the man of commerce and for the worker in the factory. For it usually happens that when nature's inner workings have once been laid bare, man sooner or later finds a way to put his brains inside the machine and to drive it whither he wills. Every increase in man's knowledge of the way in which nature works must, in the long run, increase by just so much man's ability to

control nature and to turn her hidden forces to his own account.

The purpose of this volume is to present the evidence for the atomic structure of electricity, to describe some of the most significant properties of the elementary electrical unit, the electron, and to discuss the bearing of these properties upon the two most important problems of modern physics: the structure of the atom and the nature of electromagnetic radiation. In this presentation I shall not shun the discussion of exact quantitative experiments, for it is only upon such a basis, as Pythagoras asserted more than two thousand years ago, that any real scientific treatment of physical phenomena is possible. Indeed, from the point of view of that ancient philosopher, the problem of all natural philosophy is to drive out qualitative conceptions and to replace them by quantitative relations. And this point of view has been emphasized by the farseeing throughout all the history of physics clear down to the present. One of the greatest of modern physicists, Lord Kelvin, writes:

When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science.

Although my purpose is to deal mostly with the researches of which I have had most direct and intimate knowledge, namely, those which have been carried on during the past fifteen years in this general field, first in the Ryerson Laboratory at the University of Chicago, and later at the Norman Bridge Laboratory of Physics at

the California Institute at Pasadena, I shall hope to be able to give a correct and just review of the preceding work out of which these researches grew, as well as of parallel work carried on in other laboratories. In popular writing it seems to be necessary to link every great discovery, every new theory, every important principle, with the name of a single individual. But it is an almost universal rule that developments in physics actually come about in a very different way. A science, like a plant, grows in the main by a process of infinitesimal accretion. Each research is usually a modification of a preceding one; each new theory is built like a cathedral through the addition by many builders of many different elements. This is pre-eminently true of the electron theory. It has been a growth, and I shall endeavor in every case to trace the pedigree of each research connected with it.

## CHAPTER I

### EARLY VIEWS OF ELECTRICITY

#### I. GROWTH OF THE ATOMIC THEORY OF MATTER

There is an interesting and instructive parallelism between the histories of the atomic conception of matter and the atomic theory of electricity, for in both cases the ideas themselves go back to the very beginnings of the subject. In both cases too these ideas remained absolutely sterile until the development of precise quantitative methods of measurement touched them and gave them fecundity. It took two thousand years for this to happen in the case of the theory of matter and one hundred and fifty years for it to happen in the case of electricity; and no sooner had it happened in the case of both than the two domains hitherto thought of as distinct began to move together and to appear as perhaps but different aspects of one and the same phenomenon, thus recalling again Thales' ancient belief in the essential unity of nature. How this attempt at union has come about can best be seen by a brief review of the histories of the two ideas.

The conception of a world made up of atoms which are in incessant motion was almost as clearly developed in the minds of the Greek philosophers of the School of Democritus (420 B.C.), Epicurus (370 B.C.), and Lucretius (Roman, 50 B.C.) as it is in the mind of the modern physicist, but the idea had its roots in one case in a mere speculative philosophy; in the other case, like most of



our twentieth-century knowledge, it rests upon direct, exact, quantitative observations and measurement. Not that the human eye has ever seen or indeed can ever see an individual atom or molecule. This is forever impossible, and for the simple reason that the limitations on our ability to see small objects are imposed, not by the imperfections of our instruments, but by the nature of the eye itself, or by the nature of the light-wave to which the eye is sensitive. If we are to see molecules our biological friends must develop wholly new types of eyes, viz., eyes which are sensitive to waves one thousand times shorter than those to which our present optic nerves can respond.

But after all, the evidence of our eyes is about the least reliable kind of evidence which we have. We are continually seeing things which do not exist, even though our habits are unimpeachable. It is the relations which are seen by the mind's eye to be the logical consequences of exact measurement which are for the most part dependable. So far as the atomic theory of matter is concerned, these relations have all been developed since 1800, so that both the modern atomic and the modern kinetic theories of matter, in spite of their great antiquity, are in a sense less than one hundred years old. Indeed, nearly all of our definite knowledge about molecules and atoms has come since 1851, when Joule<sup>1</sup> in England made the first absolute determination of a molecular magnitude, namely, the average speed with which gaseous molecules of a given kind are darting hither and thither at ordinary temperatures. This

<sup>1</sup> *Mem. of the Manchester Lit. and Phil. Soc.* (1851; 2d series), 107; *Phil. Mag.*, XIV (1857), 211.



result was as surprising as many others which have followed in the field of molecular physics, for it showed that this speed, in the case of the hydrogen molecule, has the stupendous value of about a mile a second. The second molecular magnitude to be found was the mean distance a molecule of a gas moves between collisions, technically called the mean free path of a molecule. This was computed first in 1860 by Clerk Maxwell.<sup>1</sup> It was also 1860 before anyone had succeeded in making any sort of an estimate of the number of molecules in a cubic centimeter of a gas. When we reflect that we can now count this number with probably greater precision than we can attain in determining the number of people living in New York, in spite of the fact that it has the huge value of 27.05 billion billion, one gains some idea of how great has been our progress in mastering some at least of the secrets of the molecular and atomic worlds. The wonder is that we got at it so late. Nothing is more surprising to the student brought up in the atmosphere of the scientific thought of the present than the fact that the relatively complex and intricate phenomena of light and electromagnetism had been built together into moderately consistent and satisfactory theories long before the much simpler phenomena of heat and molecular physics had begun to be correctly understood. And yet almost all the qualitative conceptions of the atomic and kinetic theories were developed thousands of years ago. Tyn-dall's statement of the principles of Democritus, whom Bacon considered to be "a man of mightier metal than

<sup>1</sup> *Phil. Mag.*, XIX (1860; 4th series), 28. Clausius had discussed some of the relations of this quantity in 1858 (*Pogg. Ann.*, CV [1858], 239), but Maxwell's magnificent work on the viscosity of gases first made possible its evaluation.

Plato or Aristotle, though their philosophy was noised and celebrated in the schools amid the din and pomp of professors," will show how complete an atomic philosophy had arisen 400 years B.C. "That it was entirely destroyed later was not so much due to the attacks upon it of the idealistic school, whose chief representatives were Plato and Aristotle, as to the attacks upon all civilization of Genseric, Attila, and the barbarians." That the Aristotelian philosophy lasted throughout this period is explained by Bacon thus: "At a time when all human learning had suffered shipwreck these planks of Aristotelian and Platonic Philosophy, as being of a lighter and more inflated substance, were preserved and came down to us, while things more solid sank and almost passed into oblivion."

Democritus' principles, as quoted by Tyndall, are as follows:

1. From nothing comes nothing. Nothing that exists can be destroyed. All changes are due to the combination and separation of molecules.

2. Nothing happens by chance. Every occurrence has its cause from which it follows by necessity.

3. The only existing things are the atoms and empty space; all else is mere opinion.

4. The atoms are infinite in number and infinitely various in form; they strike together and the lateral motions and whirlings which thus arise are the beginnings of worlds.

5. The varieties of all things depend upon the varieties of their atoms, in number, size, and aggregation.

6. The soul consists of fine, smooth, round atoms like those of fire. These are the most mobile of all. They interpenetrate the whole body and in their motions the phenomena of life arise.

These principles with a few modifications and omissions might almost pass muster today. The great advance which has been made in modern times is not so

much in the conceptions themselves as in the kind of foundation upon which the conceptions rest. The principles enumerated above were simply the opinions of one man or of a school of men. There were scores of other rival opinions, and no one could say which was the better. Today there is absolutely no philosophy in the field other than the atomic philosophy, at least among physicists. Yet this statement could not have been made even as much as twenty years ago. For in spite of all the multiple relationships between combining powers of the elements, and in spite of all the other evidences of chemistry and nineteenth-century physics, a group of the foremost of modern thinkers, until quite recently, withheld their allegiance from these theories. The most distinguished of this group was the German chemist and philosopher, Wilhelm Ostwald. However, in the preface to the last edition of his *Outlines of Chemistry* he now makes the following clear and frank avowal of his present position. He says:

I am now convinced that we have recently become possessed of experimental evidence of the discrete or grained nature of matter for which the atomic hypothesis sought in vain for hundreds and thousands of years. The isolation and counting of gaseous ions on the one hand . . . and on the other the agreement of the Brownian movements with the requirements of the kinetic hypothesis . . . justify the most cautious scientist in now speaking of the experimental proof of the atomic theory of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory.

## II. GROWTH OF ELECTRICAL THEORIES

The granular theory of electricity, while unlike the atomic and kinetic theories of matter in that it can boast

no great antiquity in any form, is like them in that the first man who speculated upon the nature of electricity at all conceived of it as having an atomic structure. Yet it is only within very recent years—thirty at the most—that the modern electron theory has been developed. There are no electrical theories of any kind which go back of Benjamin Franklin (1750). Aside from the discovery of the Greeks that rubbed amber had the power of attracting to itself light objects, there was no knowledge at all earlier than 1600 A.D., when Gilbert, Queen Elizabeth's surgeon, and a scientist of great genius and insight, found that a glass rod and some twenty other bodies, when rubbed with silk, act like the rubbed amber of the Greeks, and he consequently decided to describe the phenomenon by saying that the glass rod had become electrified (amberized, *electron* being the Greek word for amber), or, as we now say, had acquired a charge of electricity. In 1733 Dufay, a French physicist, further found that sealing wax, when rubbed with cat's fur, was also electrified, but that it differed from the electrified glass rod, in that it strongly attracted any electrified body which was repelled by the glass, while it repelled any electrified body which was attracted by the glass. He was thus led to recognize two kinds of electricity, which he termed "vitreous" and "resinous." About 1747 Benjamin Franklin, also recognizing these two kinds of electrification, introduced the terms "positive" and "negative," to distinguish them. Thus, he said, we will arbitrarily call any body positively electrified if it is repelled by a glass rod which has been rubbed with silk, and we will call any body negatively electrified if it is repelled by sealing wax which has been rubbed with cat's

fur. *These are today our definitions of positive and negative electrical charges.* Notice that in setting them up we propose no theory whatever of electrification, but content ourselves simply with describing the phenomena.

In the next place it was surmised by Franklin and indeed asserted by him in the very use of the terms "positive" and "negative," although the accurate proof of the relation was not made until the time of Faraday's ice-pail experiment in 1837, that when glass is positively electrified by rubbing it with silk, the silk itself takes up a negative charge of exactly the same amount as the positive charge received by the glass, and, in general, that *positive and negative electrical charges always appear simultaneously and in exactly equal amounts.*

So far, still no theory. But in order to have a rational explanation of the phenomena so far considered, particularly this last one, Franklin now made the assumption that something which he chose to call the electrical fluid or "electrical fire" exists in normal amount as a constituent of all matter in the neutral, or unelectrified state, and that more than the normal amount in any body is manifested as a positive electrical charge, and less than the normal amount as a negative charge. Aepinus, professor of physics at St. Petersburg and an admirer of Franklin's theory, pointed out that, in order to account for the repulsion of two negatively electrified bodies, it was necessary to assume that matter, when divorced from Franklin's electrical fluid, was self-repellent, i.e., that it possessed properties quite different from those which are found in ordinary unelectrified matter. In order, however, to leave matter, whose independent existence was thus threatened, endowed with its familiar old properties,



and in order to get electrical phenomena into a class by themselves, other physicists of the day, led by Symmer, 1759, preferred to assume that *matter in a neutral state shows no electrical properties because it contains as constituents equal amounts of two weightless fluids which they called positive and negative electricity, respectively*. From this point of view a positively charged body is one in which there is more of the positive fluid than of the negative, and a negatively charged body is one in which the negative fluid is in excess.

Thus arose the so-called two-fluid theory—a theory which divorced again the notions of electricity and matter after Franklin had taken a step toward bringing them together. This theory, in spite of its intrinsic difficulties, dominated the development of electrical science for one hundred years and more. This was because, if one did not bother himself much with the underlying physical conception, the theory lent itself admirably to the description of electrical phenomena and also to mathematical formulation. Further, it was convenient for the purposes of classification. It made it possible to treat electrical phenomena in a category entirely by themselves, without raising any troublesome questions as to the relation, for example, between electrical and gravitational or cohesive forces. But in spite of these advantages it was obviously a makeshift. For the notion of two fluids which could exert powerful forces and yet which were absolutely without weight—the most fundamental of physical properties—and the further notion of two fluids which had no physical properties whatever, that is, which disappeared entirely when they were mixed in equal proportions—these notions were in a

high degree non-physical. Indeed, Sir J. J. Thomson remarked in his Silliman Lectures in 1903 that

the physicists and mathematicians who did most to develop the fluid theories confined their attention to questions which involved only the law of forces between electrified bodies and the simultaneous production of equal quantities of plus and minus electricity, and refined and idealized their conception of the fluids themselves until any reference to their physical properties was considered almost indelicate.

From the point of view of economy in hypothesis, Franklin's one-fluid theory, as modified by Aepinus, was the better. Mathematically the two theories were identical. The differences may be summed up thus. The modified one-fluid theory required that matter, when divorced from the electrical fluid, have exactly the same properties which the two-fluid theory ascribed to negative electricity, barring only the property of fluidity. So that the most important distinction between the theories was that the two-fluid theory assumed the existence of three distinct entities, named positive electricity, negative electricity, and matter, while the one-fluid theory reduced these three entities to two, which Franklin called matter and electricity, but which might perhaps as well have been called positive electricity and negative electricity, unelectrified matter being reduced to a mere combination of these two.

Of course, the idea of a granular structure for electricity was foreign to the two-fluid theory, and since this dominated the development of electrical science, there was seldom any mention in connection with it of an electrical atom, even as a speculative entity. But with Franklin the case was different. His theory was essen-



tially a material one, and he unquestionably believed in the existence of an electrical particle or atom, for he says: "The electrical matter consists of particles extremely subtle, since it can permeate common matter, even the densest, with such freedom and ease as not to receive any appreciable resistance." When Franklin wrote that, however, he could scarcely have dreamed that it would ever be possible to isolate and study by itself one of the ultimate particles of the electrical fluid. The atomic theory of electricity was to him what the atomic theory of matter was to Democritus, a pure speculation.

The first bit of experimental evidence which appeared in its favor came in 1833, when Faraday found that the passage of a given quantity of electricity through a solution containing a compound of hydrogen, for example, would always cause the appearance at the negative terminal of the same amount of hydrogen gas irrespective of the kind of hydrogen compound which had been dissolved, and irrespective also of the strength of the solution; that, further, the quantity of electricity required to cause the appearance of one gram of hydrogen would always deposit from a solution containing silver exactly 107.1 grams of silver. This meant, since the weight of the silver atom is exactly 107.1 times the weight of the hydrogen atom, that the hydrogen atom and the silver atom are associated in the solution with exactly the same quantity of electricity. When it was further found in this way that all atoms which are univalent in chemistry, that is, which combine with one atom of hydrogen, carry precisely the same quantity of electricity, and all atoms which are bivalent carry twice

this amount, and, in general, that valency, in chemistry, is always exactly proportional to the quantity of electricity carried by the atom in question, it was obvious that the atomic theory of electricity had been given very strong support.

But striking and significant as were these discoveries, they did not serve at all to establish the atomic hypothesis of the nature of electricity. They were made at the very time when attention began to be directed strongly away from the conception of electricity as a substance of any kind, and it was no other than Faraday himself who, in spite of the brilliant discoveries just mentioned, started this second period in the development of electrical theory, a period lasting from 1840 to about 1900. In this period electrical phenomena are almost exclusively thought of in terms of stresses and strains in the medium which surrounds the electrified body. Up to this time a more or less definite something called a charge of electricity had been thought of as existing *on* a charged body and had been imagined to exert forces on other charged bodies at a distance from it in quite the same way in which the gravitational force of the earth acts on the moon or that of the sun on the earth. This notion of action at a distance was repugnant to Faraday, and he found in the case of electrical forces experimental reasons for discarding it which had not then, nor have they as yet, been found in the case of gravitational forces. These reasons are summed up in the statement that the electrical force between two charged bodies is found to depend on the nature of the intervening medium, while gravitational pulls are, so far as is known, independent of intervening bodies. Faraday, therefore, pictured to himself

the intervening medium as transmitting electrical force in quite the same way in which an elastic deformation started at one end of a rod is transmitted by the rod. Further, since electrical forces act through a vacuum, Faraday had to assume that it is the ether which acts as the transmitter of these electrical stresses and strains. The properties of the ether were then conceived of as modified by the presence of matter in order to account for the fact that the same two charges attract each other with different forces according as the intervening medium is, for example, glass, or ebonite, or air, or merely ether. These views, conceived by Faraday and put into mathematical form by Maxwell, called attention away from the electrical phenomena in or on a conductor carrying electricity and focused it upon the stresses and strains taking place in the medium about the conductor. When in 1886 Heinrich Hertz in Bonn, Germany, proved by direct experiment that electrical forces are indeed transmitted in the form of electric waves, which travel through space with the speed of light exactly as the Faraday-Maxwell theory had predicted, the triumph of the ether-stress point of view was complete. Thereupon textbooks were written by enthusiastic, but none too cautious, physicists in which it was asserted that an electric charge is nothing more than a "state of strain in the ether," and an electric current, instead of representing the passage of anything definite along the wire, corresponds merely to a continuous "slip" or "break-down of a strain" in the medium within the wire. Sir Oliver Lodge's early book, *Modern Views of Electricity*, was perhaps the most influential disseminator and expounder of this point of view.

Now what had actually been proved was not that electricity is a state of strain, but that when any electrical charge appears upon a body the medium about the body does indeed become the seat of new forces which are transmitted through the medium, like any elastic forces, with a definite speed. Hence it is entirely proper to say that the medium about a charged body is in a state of strain. But it is one thing to say that the electrical charge on the body *produces* a state of strain in the surrounding medium, and quite another thing to say that the electrical charge *is nothing but* a state of strain in the surrounding medium, just as it is one thing to say that when a man stands on a bridge he produces a mechanical strain in the timbers of the bridge, and another thing to say that the man is nothing more than a mechanical strain in the bridge. The practical difference between the two points of view is that in the one case you look for other attributes of the man besides the ability to produce a strain in the bridge, and in the other case you do not look for other attributes. So the strain theory, although not irreconcilable with the atomic hypothesis, was actually antagonistic to it, because it led men to think of the strain as distributed continuously about the surface of the charged body, rather than as radiating from definite spots or centers peppered over the surface of the body. Between 1833 and 1900, then, the physicist was in this peculiar position: when he was thinking of the passage of electricity through a solution, he for the most part, following Faraday, pictured to himself definite specks or atoms of electricity as traveling through the solution, each atom of matter carrying an exact multiple, which might be anywhere between one and eight, of a

definite elementary electrical atom, while, when he was thinking of the passage of a current through a metallic conductor, he gave up altogether the atomic hypothesis, and attempted to picture the phenomenon to himself as a continuous "slip" or "breakdown of a strain" in the material of the wire. In other words, he recognized two types of electrical conduction which were wholly distinct in kind—electrolytic conduction and metallic conduction; and since more of the problems of the physicist dealt with metallic than with electrolytic conduction, the atomic conception, as a general hypothesis, was almost, though not quite, unheard of. Of course it would be unjust to the thinkers of this period to say that they failed to recognize and appreciate this gulf between current views as to the nature of electrolytic and metallic conduction, and simply ignored the difficulty. This they did not do, but they had all sorts of opinions as to the causes. Maxwell himself in his text on *Electricity and Magnetism*, published in 1873, recognizes, in the chapter on "Electrolysis,"<sup>1</sup> the significance of Faraday's laws, and even goes so far as to say that "for convenience in description we may call this constant molecular charge (revealed by Faraday's experiments) one molecule of electricity." Nevertheless, a little farther on he repudiates the idea that this term can have any physical significance by saying that "it is extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges, for then we shall have obtained a secure basis on which to form a true theory of electric currents and so become independent of these provisional hypotheses."

<sup>1</sup> I, 375-86.



And as a matter of fact, Faraday's experiments had not shown at all that electrical charges on metallic conductors consist of specks of electricity, even though they had shown that the charges on ions in solutions have definite values which are always the same for univalent ions. It was entirely logical to assume, as Maxwell did, that an ion took into solution a definite quantity of electricity because of some property which it had of always charging up to the same amount from a charged plate. There was no reason for assuming the charge *on the electrode* to be made up of some exact number of electrical atoms.

On the other hand, Wilhelm Weber, in papers written in 1871,<sup>1</sup> built up his whole theory of electromagnetism on a basis which was practically identical with the modified Franklin theory and explained all the electrical phenomena exhibited by conductors, including thermoelectric and Peltier effects, on the assumption of two types of electrical constituents of atoms, one of which was very much more mobile than the other. Thus the hypothetical molecular current, which Ampere had imagined fifty years earlier to be continually flowing inside of molecules and thereby rendering these molecules little electromagnets, Weber definitely pictures to himself as the rotation of light, positive charges about heavy negative ones. His words are:

The relation of the two particles as regards their motions is determined by the ratio of their masses  $e$  and  $e'$ , on the assumption that in  $e$  and  $e'$  are included the masses of the ponderable atoms which are attached to the electrical atoms. Let  $e$  be the positive electrical particle. Let the negative be exactly equal and opposite

<sup>1</sup> See *Werke*, IV, 281.

and therefore denoted by  $-e$  (instead of  $e'$ ). But let a ponderable atom be attracted to the latter so that its mass is thereby so greatly increased as to make the mass of the positive particle vanishingly small in comparison. The particle  $-e$  may then be thought of as at rest and the particle  $+e$  as in motion about the particle  $-e$ . The two unlike particles in the condition described constitute then an Amperian molecular current.

It is practically this identical point of view which has been elaborated and generalized by Lorentz and others within the past three decades in the development of the modern electron theory, with this single difference, that we now have experimental proof that it is the negative particle whose mass or inertia is negligible in comparison with that of the positive instead of the reverse. Weber even went so far as to explain thermoelectric and Peltier effects by differences in the kinetic energies in different conductors of the electrical particles.<sup>1</sup> Nevertheless his explanations are here widely at variance with our modern conceptions of heat.

Again, in a paper read before the British Association at Belfast in 1874, G. Johnstone Stoney not only stated clearly the atomic theory of electricity, but actually went so far as to estimate the value of the elementary electrical charge, and he obtained a value which was about as reliable as any which had been found until within quite recent years. He got, as will be more fully explained in the next chapter,  $.3 \times 10^{-10}$  absolute electrostatic units, and he got this result from the amount of electricity necessary to separate from a solution one gram of hydrogen, combined with kinetic theory estimates as to the number of atoms of hydrogen in two grams, i.e., in one

<sup>1</sup> *Op. cit.*, p. 294.

gram molecule of that element. This paper was entitled, "On the Physical Units of Nature," and though read in 1874 it was not published in full until 1881.<sup>1</sup> After showing that all physical measurements may be expressed in terms of three fundamental units, he asserts that it would be possible to replace our present purely arbitrary units (the centimeter, the gram, and the second) by three natural units, namely, the velocity of light, the coefficient of gravitation, and the elementary electrical charge. With respect to the last he says:

Finally nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's law in the following terms, which, as I shall show, will give it precision, viz.: *For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases.* This definite quantity of electricity I shall call  $E_r$ . If we make this our unit of electricity, we shall probably have made a very important step in our study of molecular phenomena.

Hence we have very good reason to suppose that in  $V_r$ ,  $G_r$ , and  $E_r$ , we have three of a series of systematic units that in an eminent sense are the units of nature, and stand in an intimate relation with the work which goes on in her mighty laboratory.

Take one more illustration from prominent writers of this period. In his Faraday lecture delivered at the Royal Institution in 1881, Helmholtz spoke as follows:

Now the most startling result of Faraday's law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity.<sup>2</sup>

<sup>1</sup> *Phil. Mag.*, XI (1881; 5th series), 384.

<sup>2</sup> *Wissenschaftliche Abhandlungen*, III, 69.



This looks like a very direct and unequivocal statement of the atomic theory of electricity, and yet in the same lecture Helmholtz apparently thinks of metallic conduction as something quite different from electrolytic when he says:

All these facts show that electrolytic conduction is not at all limited to solutions of acids or salts. It will, however, be rather a difficult problem to find out how far the electrolytic conduction is extended, and I am not yet prepared to give a positive answer.

The context shows that he thought of extending the idea of electrolytic conduction to a great many insulators. But there is no indication that he thought of extending it to metallic conductors and imagining these electrical atoms as existing as discrete individual things on charged metals or as traveling along a wire carrying an electrical current. Nevertheless, the statement quoted above is one of the most unequivocal which can be found anywhere up to about 1899 as to the atomic nature of electricity.

The foregoing quotations are sufficient to show that the atomic theory of electricity, like the atomic theory of matter, is not at all new so far as the conception alone is concerned. In both cases there were individuals who held almost exactly the modern point of view. In both cases, too, the chief new developments have consisted in the appearance of new and exact *experimental* data which has silenced criticism and compelled the abandonment of other points of view which up to about 1900 flourished along with, and even more vigorously than, the atomic conception. Even in 1897 Lord Kelvin, with a full knowledge of all the new work which was appearing on X-rays and cathode rays, could seriously raise the

question whether electricity might not be a "continuous homogeneous liquid." He does it in these words:

Varley's fundamental discovery of the cathode rays, splendidly confirmed and extended by Crookes, seems to me to necessitate the conclusion that resinous electricity, not vitreous, is *The Electric Fluid*, if we are to have a one-fluid theory of electricity. Mathematical reasons prove that if resinous electricity is a continuous homogeneous liquid it must, in order to produce the phenomena of contact electricity, which you have seen this evening, be endowed with a cohesional quality. It is just conceivable, though it does not at present seem to me very probable, that this idea may deserve careful consideration. I leave it, however, for the present and prefer to consider an atomic theory of electricity foreseen as worthy of thought by Faraday and Clerk-Maxwell, very definitely proposed by Helmholtz in his last lecture to the Royal Institution, and largely accepted by present-day workers and teachers. Indeed Faraday's laws of electrolysis seem to necessitate something atomic in electricity, . . . .<sup>1</sup>

What was the new experimental work which already in 1897 was working this change in viewpoint? Much of it was at first little if at all more convincing than that which had been available since Faraday's time. Nevertheless it set physicists to wondering whether stresses and strains in the ether had not been a bit overworked, and whether in spite of their undoubted existence electricity itself might not after all be something more definite, more material, than the all-conquering Maxwell theory had assumed it to be.

The result of the past twenty-five years has been to bring us back very close to where Franklin was in 1750, with the single difference that our modern electron theory rests upon a mass of very direct and convincing evidence, which it is the purpose of the next chapters to present.

<sup>1</sup> Kelvin, "Contact Electricity and Electrolysis," *Nature*, LVI (1897), 84.

## CHAPTER II

### THE EXTENSION OF THE ELECTROLYTIC LAWS TO CONDUCTION IN GASES

#### I. THE ORIGIN OF THE WORD "ELECTRON"

The word "electron" was first suggested in 1891 by Dr. G. Johnstone Stoney as a name for the "natural unit of electricity," namely, that quantity of electricity which must pass through a solution in order to liberate at one of the electrodes one atom of hydrogen or one atom of any univalent substance. In a paper published in 1891 he says:

Attention must be given to Faraday's Law of Electrolysis, which is equivalent to the statement that in electrolysis a definite quantity of electricity, the same in all cases, passes for each chemical bond that is ruptured. The author called attention to this form of the law in a communication made to the British Association in 1874 and printed in the *Scientific Proceedings of the Royal Dublin Society* of February, 1881, and in the *Philosophical Magazine* for May, 1881, pp. 385 and 386 of the latter. It is there shown that the amount of this very remarkable quantity of electricity is about the twentietheth ( $\text{that is } \frac{1}{10^{20}}$ ) of the usual electromagnetic unit of electricity, i.e., the unit of the Ohm series. This is the same as 3 eleventheths ( $\frac{3}{10^{11}}$ ) of the much smaller C.G.S. electrostatic unit of quantity. A charge of this amount is associated in the chemical atom with each bond. There may accordingly be several such charges in one chemical atom, and there appear to be at least two in each atom. These charges, which it will be convenient to call "electrons," cannot be removed from the atom, but they become disguised when atoms chemically unite. If an

electron be lodged at the point  $P$  of the molecule which undergoes the motion described in the last chapter, the revolution of this charge will cause an electromagnetic undulation in the surrounding ether.<sup>1</sup>

It will be noticed from this quotation that the word "electron" was introduced to denote simply a definite elementary quantity of electricity without any reference to the mass or inertia which may be associated with it, and Professor Stoney implies that every atom must contain at least two electrons, one positive and one negative, because otherwise it would be impossible that the atom as a whole be electrically neutral. As a matter of fact the evidence is now altogether convincing that the hydrogen atom does indeed contain just one positive and one negative electron.

It is unfortunate that all writers have not been more careful to retain the original significance of the word introduced by Professor Stoney, for it is obvious that a word is needed which denotes merely the elementary unit of electricity and has no necessary implication as to where that unit is found, to what it is attached, with what inertia it is associated, or whether it is positive or negative in sign; and it is also apparent that the word "electron" is the logical one to associate with this conception. Further, there is no difficulty in retaining this original and derivative significance of the word "electron," and at the same time permitting its common use as a convenient abridgment for "the free negative electron." In other words, in view of the omnipresence of the negative electron in experimental physics and the extreme rarity of

<sup>1</sup> *Scientific Transactions of the Royal Dublin Society*, IV (1891; 11th series), 563.

the isolated positive electron, it may be generally agreed that the negative is understood unless the positive is specified. The case is then in every way identical with that found in the use of the word "man," which serves admirably both to designate the genus "homo" and also to denote the male representative of that genus, the female being then differentiated by the use of a prefix. The terms "electron" and "positive electron" would then be used altogether conveniently precisely as are the terms "man" and "woman." Indeed, the most authoritative writers—Thomson, Rutherford, Campbell, Richardson, etc.—have in fact retained the original significance of the word "electron" instead of using it to denote *solely* the free negative electron, the mass of which is  $1/1,845$  of that of the hydrogen atom. All of these writers in books or articles written since 1913<sup>1</sup> have treated of positive as well as negative electrons, although the mass associated with the former is never less than that of the hydrogen atom. Nor is this altogether logical use confined at all to English. Prenin has approved it, and Nernst in the 1921 edition of his *Theoretische Chemie*, on pp. 197 and 456, definitely and unambiguously defines the positive and negative electrons, precisely as has been done above, as the elementary positive and negative electrical charges, respectively.

## II. THE DETERMINATION OF $\frac{e}{m}$ AND $Ne$ FROM THE FACTS OF ELECTROLYSIS

Faraday's experiments had of course not furnished the data for determining anything about how much

<sup>1</sup> See particularly Rutherford's presidential address at the recent Liverpool meeting of the British Association, *Science*, LVIII (1923), 213.

electricity an electron represents in terms of the standard unit by which electrical charges are ordinarily measured in the laboratory. This is called the coulomb, and represents the quantity of electricity conveyed in one second by one ampere. Faraday had merely shown that a given current flowing in succession through solutions containing different univalent elements like hydrogen or silver or sodium or potassium would deposit weights of these substances which are exactly proportional to their respective atomic weights. This enabled him to assert that one and the same amount of electricity is associated in the process of electrolysis with an atom of each of these substances. He thought of this charge as carried by the atom, or in some cases by a group of atoms, and called the group with its charge an "ion," that is, a "goer," or "traveler." Just how the atoms come to be charged in a solution Faraday did not know, nor do we know now with any certainty. Further, we do not know how much of the solvent an ion associates with itself and drags with it through the solution. But we do know that when a substance like salt is dissolved in water many of the neutral  $\text{NaCl}$  molecules are split up by some action of the water into positively charged sodium ( $\text{Na}$ ) ions and negatively charged chlorine ( $\text{Cl}$ ) ions. The ions of opposite sign doubtless are all the time recombining, but others are probably continually forming, so that at each instant there are many uncombined ions. Again, we know that when a water solution of copper sulphate is formed many of the neutral  $\text{CuSO}_4$  molecules are split up into positively charged  $\text{Cu}$  ions and negatively charged  $\text{SO}_4$  ions. In this last case too we find that the same current which will deposit in a



given time from a silver solution a weight of silver equal to its atomic weight will deposit from the copper-sulphate solution in the same time a weight of copper equal to exactly one-half its atomic weight. Hence we know that the copper ion carries in solution twice as much electricity as does the silver ion, that is, it carries a charge of two electrons.

But though we could get from Faraday's experiments no knowledge about the quantity of electricity,  $e$ , represented by one electron, we could get very exact information about the ratio of the ionic charge  $E$  to the mass of the atom with which it is associated in a given solution.

For, if the whole current which passes through a solution is carried by the ions—and if it were not we should not always find the deposits exactly proportional to atomic weights—then the ratio of the total quantity of electricity passing to the weight of the deposit produced must be the same as the ratio of the charge  $E$  on each ion to the mass  $m$  of that ion. But by international agreement one absolute unit of electricity has been defined in the electromagnetic system of units as the amount of electricity which will deposit from a silver solution 0.01118 grams of metallic silver. Hence if  $m$  refers to the silver ion and  $E$  means the charge on the ion, we have

$$\text{for silver } \frac{E}{m} = \frac{1}{0.01118} = 89.44 \text{ electromagnetic units;}$$

or if  $m$  refers to the hydrogen ion, since the atomic weight of silver is  $\frac{107.88}{1.008}$  times that of hydrogen,

$$\text{for hydrogen } \frac{E}{m} = \frac{1}{0.01118} \times \frac{107.88}{1.008} = 9,573,$$

which is about  $10^4$  electromagnetic units.

Thus in electrolysis  $\frac{E}{m}$  varies from ion to ion, being for univalent ions, for which  $E$  is the same and equal to one electron  $e$ , inversely proportional to the atomic weight of the ion. For polyvalent ions  $E$  may be 2, 3, 4, or 5 electrons, but since hydrogen is at least 7 times lighter than any other ion which is ever found in solution, and its charge is but one electron, we see that the largest value which  $\frac{E}{m}$  ever has in electrolysis is its value for hydrogen, namely, about  $10^4$  electromagnetic units.

Although  $\frac{E}{m}$  varies with the nature of the ion, there is a quantity which can be deduced from it which is a universal constant. This quantity is denoted by  $Ne$ , where  $e$  means as before an electron and  $N$  is the Avogadro constant or the number of molecules in 16 grams of oxygen, i.e., in one gram molecule. We can get this at once from the value of  $\frac{E}{m}$  by letting  $m$  refer to the mass of that imaginary univalent atom which is the unit of our atomic weight system, namely, an atom which is exactly  $1/16$  as heavy as oxygen or  $1/107.88$  as heavy as silver. For such an atom

$$\frac{E}{m} = \frac{e}{m} = \frac{107.88}{0.01118} = 9649.4.$$

Multiplying both numerator and denominator by  $N$  and remembering that for this gas one gram molecule means 1 gram, that is  $Nm = 1$ , we have

$$Ne = 9649.4 \text{ absolute electromagnetic units, } \dots \dots (1)$$



and since the electromagnetic unit is equivalent to  $3 \times 10^{10}$  electrostatic units, we have

$$Ne = 28,948 \times 10^{16} \text{ absolute electrostatic units.}$$

Further, since a gram molecule of an ideal gas under standard conditions, i.e., at  $0^\circ \text{C}$ . 76 cm. pressure, occupies 22412 c.c., if  $n_1$  represents the number of molecules of such a gas per cubic centimeter at  $0^\circ \text{C}$ ., 76 cm., we have

$$n_1 e = \frac{28,948 \times 10^{16}}{22,412} = 1.292 \times 10^{10} \text{ electrostatic units.}$$

Or if  $n$  represent the number of molecules per cubic centimeter at  $15^\circ \text{C}$ . 76 cm., we should have to multiply the last number by the ratio of absolute temperatures, i.e., by  $273/288$  and should obtain then

$$ne = 1.225 \times 10^{10} \dots \dots \dots (2)$$

Thus, even though the facts of electrolysis give us no information at all as to how much of a charge one electron  $e$  represents, they do tell us very exactly that if we should take  $e$  as many times as there are molecules in a gram molecule we should get exactly 9,650 absolute electromagnetic units of electricity. This is the amount of electricity conveyed by a current of 1 ampere in 10 seconds. Until quite recently we have been able to make nothing better than rough guesses as to the number of molecules in a gram molecule, but with the aid of these guesses, obtained from the Kinetic Theory, we have, of course, been enabled by (1) to make equally good guesses about  $e$ . Those guesses, based for the most part on quite uncertain computations as to the average

radius of a molecule of air, placed  $N$  anywhere between  $2 \times 10^{23}$  and  $20 \times 10^{23}$ . It was in this way that G. Johnstone Stoney in 1874 estimated  $e$  at  $.3 \times 10^{-10}$  E.S. units. In O. E. Meyer's *Kinetische Theorie der Gase* (p. 335; 1899),  $n$ , the number of molecules in a cubic centimeter, is given as  $6 \times 10^{19}$ . This would correspond to  $e = 2 \times 10^{-10}$ . In all this  $e$  is the charge carried by a univalent ion in solution and  $N$  or  $n$  is a pure number, which is a characteristic gas constant, it is true, but the analysis has nothing whatever to do with gas conduction.

### III. THE NATURE OF GASEOUS CONDUCTION

The question whether gases conduct at all, and if so, whether their conduction is electrolytic or metallic or neither, was scarcely attacked until about 1895. Coulomb in 1785 had concluded that after allowing for the leakage of the supports of an electrically charged conductor, some leakage must be attributed to the air itself, and he explained this leakage by assuming that the air molecules became charged by contact and were then repelled—a wholly untenable conclusion, since, were it true, no conductor in air could hold a charge long even at low potentials, nor could a very highly charged conductor lose its charge very rapidly when charged above a certain potential and then when the potential fell below a certain critical value cease almost entirely to lose it. This is what actually occurs. Despite the erroneousness of this idea, it persisted in textbooks written as late as 1900.

Warburg in 1872 experimented anew on air leakage and was inclined to attribute it all to dust particles. The real explanation of gas conduction was not found until

after the discovery of X-rays in 1895. The convincing experiments were made by J. J. Thomson, or at his instigation in the Cavendish Laboratory at Cambridge, England. The new work grew obviously and simply out of the fact that X-rays, and a year or two later radium rays, were found to discharge an electroscope, i.e., to produce conductivity in a gas. Theretofore no agencies had been known by which the electrical conductivity of a gas could be controlled at will.

Thomson and his pupils found that the conductivity induced in gases by X-rays disappeared when the gas was sucked through glass wool.<sup>1</sup> It was also found to be reduced when the air was drawn through narrow metal tubes. Furthermore, it was removed entirely by passing the stream of conducting gas between plates which were maintained at a sufficiently large potential difference. The first two experiments showed that the conductivity was due to something which could be removed from the gas by filtration, or by diffusion to the walls of a metal tube; the last proved that this something was electrically charged.

When it was found, further, that the electric current obtained from air existing between two plates and traversed by X-rays rose to a maximum as the P.D. between the plates increased, and then reached a value which was thereafter independent of this potential difference; and, further, that this conductivity of the air died out slowly through a period of several seconds when the X-ray no longer acted, it was evident that the qualitative proof was complete that gas conduction must be due to charged particles produced in the

<sup>1</sup> J. J. Thomson and E. Rutherford, *Phil. Mag.*, XLII (1896), 392.

air at a definite rate by a constant source of X-rays, and that these charged particles, evidently of both plus and minus signs, disappear by recombination when the rays are removed. The maximum or *saturation* currents which could be obtained when a given source was ionizing the air between two plates whose potential difference could be varied were obviously due to the fact that when the electric field between the plates became strong enough to sweep all the ions to the plates as fast as they were formed, none of them being lost by diffusion or recombination, the current obtained could, of course, not be increased by further increase in the field strength. Thus gas conduction was definitely shown about 1896 to be electrolytic in nature.

#### IV. COMPARISON OF THE GASEOUS ION AND THE ELECTROLYTIC ION

But what sort of ions were these that were thus formed? We did not know the absolute value of the charge on a univalent ion in electrolysis, but we did know accurately *ne*. Could this be found for the ions taking part in gas conduction? That this question was answered affirmatively was due to the extraordinary insight and resourcefulness of J. J. Thomson and his pupils at the Cavendish Laboratory in Cambridge, both in working out new theoretical relations and in devising new methods for attacking the new problems of gaseous conduction. These workers found first a method of expressing the quantity *ne* in terms of two measurable constants, called (1) the mobility of gaseous ions and (2) the coefficient of diffusion of these ions. Secondly, they devised new methods of measuring these two

constants—constants which had never before been determined. The theory of the relation between these constants and the quantity  $ne$  will be found in Appendix A. The result is

$$ne = \frac{v_0}{D} P \dots\dots\dots (3)$$

in which  $P$  is the pressure existing in the gas and  $v_0$  and  $D$  are the mobility and the diffusion coefficients respectively of the ions at this pressure.

If then we can find a way of measuring the mobilities  $v_0$  of atmospheric ions and also the diffusion coefficients  $D$ , we can find the quantity  $ne$ , in which  $n$  is a mere number, viz., the number of molecules of air per cubic centimeter at  $15^\circ \text{C.}$ , 76 cm. pressure, and  $e$  is the average charge on an atmosphere ion. We shall then be in position to compare this with the product we found in (2) on p. 31, in which  $n$  had precisely the same significance as here, but  $e$  meant the average charge carried by a univalent ion in electrolysis.

The methods devised in the Cavendish Laboratory between 1897 and 1903 for measuring the mobilities and the diffusion coefficients of gaseous ions have been used in all later work upon these constants. The mobilities were first determined by Rutherford in 1897,<sup>1</sup> then more accurately by another method in 1898.<sup>2</sup> Zeleny devised a quite distinct method in 1900,<sup>3</sup> and Langevin still another method in 1903.<sup>4</sup> These observers all agree closely in finding the average mobility (velocity in unit

<sup>1</sup> *Phil. Mag.*, XLIV (1898), 422.

<sup>2</sup> *Proc. Camb. Phil. Soc.*, IX, 401.

<sup>3</sup> *Phil. Trans.*, A 195, p. 193.

<sup>4</sup> *Annale de Chimie et de Physique*, XXVIII, 289.

field) of the negative ion in dry air about 1.83 cm. per second, while that of the positive ion was found but 1.35 cm. per second. In hydrogen these mobilities were about 7.8 cm. per second and 6.1 cm. per second, respectively, and in general the mobilities in different gases, though not in vapors, seem to be roughly in the inverse ratio of the square roots of the molecular weights.

The diffusion coefficients of ions were first measured in 1900 by Townsend, now professor of physics in Oxford, England,<sup>1</sup> by a method devised by him and since then used by other observers in such measurements. If we denote the diffusion coefficient of the positive ion by  $D+$  and that of the negative by  $D-$ , Townsend's results in dry air may be stated thus:

$$\begin{aligned} D+ &= 0.028 \\ D- &= 0.043. \end{aligned}$$

These results are interesting in two respects. In the first place, they seem to show that for some reason the positive ion in air is more sluggish than the negative, since it travels but about 0.7 ( $=1.35/1.81$ ) as fast in a given electrical field and since it diffuses through air but about 0.7 ( $=28/43$ ) as rapidly. In the second place, the results of Townsend show that an ion is very much more sluggish than is a molecule of air, for the coefficient of diffusion of oxygen through air is 0.178, which is four times the rate of diffusion of the negative ion through air and five times that of the positive ion. This sluggishness of ions as compared with molecules was at first universally considered to mean that the gaseous ion is not a single molecule with an attached electrical charge, but

<sup>1</sup> *Phil. Trans.*, A 193, p. 129.



a cluster of perhaps from three to twenty molecules held together by such a charge. If this is the correct interpretation, then for some reason the positive ion in air is a larger cluster than is the negative ion.

It has been since shown by a number of observers that the ratio of the mobilities of the positive and negative ions is not at all the same in other gases as it is in air. In carbon dioxide the two mobilities have very nearly the same value, while in chlorine, water vapor, and the vapor of alcohol the positive ion apparently has a slightly larger mobility than the negative. There seems to be some evidence that the negative ion has the larger mobility in gases which are electro-positive, while the positive has the larger mobility in the gases which are strongly electro-negative. This dependence of the ratio of mobilities upon the electro-positive or electro-negative character of the gas has usually been considered strong evidence in favor of the cluster-ion theory.

Very recently, however, Loeb,<sup>1</sup> who has worked at the Ryerson Laboratory on mobilities in powerful electric fields, and Wellish,<sup>2</sup> who, at Yale, has measured mobilities at very low pressures, have concluded that their results are not consistent with the cluster-ion theory, but must rather be interpreted in terms of the so-called Atom-ion Theory. This theory seeks to explain the relative sluggishness of ions, as compared with molecules, by the additional resistance which the gaseous medium offers to the motion of a molecule through it when that

<sup>1</sup> Leonard B. Loeb, *Proc. Nat. Acad.*, II (1916), 345, and *Phys. Rev.*, 1917.

<sup>2</sup> Wellish, *Amer. Jour. of Science*, XXXIX (1915), 583.

molecule is electrically charged. *According to this hypothesis, the ion would be simply an electrically charged molecule.*

So far as the negative ion is concerned, the situation at the moment seems to be in favor of the atom-ion theory. There has recently developed strong evidence<sup>1</sup> that although in some very pure gases, such as helium, argon, and even nitrogen, the negative electron cannot find attachment at all, when it does attach so as to form ions of the mobility mentioned above, it carries with it thereafter but a single molecule.

On the other hand, Erikson<sup>2</sup> and Wahlin<sup>3</sup> have apparently shown quite conclusively that if the mobility of the positive ion in air is measured within .03 second of the time of its formation, its value is identical with that of the negative, namely, 1.8 cm. per second, while a short time thereafter it has sunk to about 1.4 cm. per second because of the addition of one more molecule, thus forming a very stable two-molecule-ion group.

Fortunately, the quantitative evidence for the electrolytic nature of gas conduction is in no way dependent upon the correctness of either one of the theories as to the nature of the ion. It depends simply upon the comparison of the values of  $ne$  obtained from electrolytic measurements, and those obtained from the substitution in equation (3) of the measured values of  $v_0$  and  $D$  for gaseous ions.

As for these measurements, results obtained by Franck and Westphal,<sup>4</sup> who in 1908 repeated in Berlin

<sup>1</sup> L. B. Loeb, *Jour. Franklin Inst.*, CXC VII (1924), 45.

<sup>2</sup> H. A. Erikson, *Phys. Rev.*, XX (1922), 1118.

<sup>3</sup> H. B. Wahlin, *ibid.*, p. 267.

<sup>4</sup> *Verh. der deutsch. phys. Ges.*, XI (1909), 146 and 276.



both measurements on diffusion coefficients and mobility coefficients, agree within 4 or 5 per cent with the results published by Townsend in 1900. According to both of these observers, the value of  $ne$  for the negative ions produced in gases by X-rays, radium rays, and ultra-violet light came out, within the limits of experimental error, which were presumably 5 or 6 per cent, the same as the value found for univalent ions in solutions, namely,  $1.23 \times 10^{10}$  absolute electrostatic units. This result seems to show with considerable certainty that the negative ions in gases ionized by X-rays or similar agencies carry on the average the same charge as that borne by the univalent ion in electrolysis. When we consider the work on the positive ion, our confidence in the inevitableness of the conclusions reached by the methods under consideration is perhaps somewhat shaken. For Townsend found that the value of  $ne$  for the positive ion came out about 14 per cent higher than the value of this quantity for the univalent ion in electrolysis, a result which he does not seem at first to have regarded as inexplicable on the basis of experimental uncertainties in his method. In 1908, however,<sup>1</sup> he devised a second method of measuring the ratio of the mobility and the diffusion coefficient and obtained this time, as before, for the negative ion,  $ne = 1.23 \times 10^{10}$ , but for the positive ion twice that amount, namely,  $2.46 \times 10^{10}$ . From these last experiments he concluded that the positive ions in gases ionized by X-rays carried on the average twice the charge carried by the univalent ion in electrolysis. Franck and Westphal, however, found in their work that Townsend's original value for  $ne$  for the

<sup>1</sup> *Proc. Roy. Soc.*, LXXX (1908), 207.

positive ions was about right, and hence concluded that only about 9 per cent of the positive ions could carry a charge of value  $2e$ . Work which will be described later indicates that neither Townsend's nor Franck and Westphal's conclusions are correct, and hence point to errors of some sort in both methods. But despite these difficulties with the work on positive ions, it should nevertheless be emphasized that Townsend was the first to bring forward strong quantitative evidence (1) that the mean charge carried by the negative ions in ionized gases is the same as the mean charge carried by univalent ions in solutions, and (2) that the mean charge carried by the positive ions in gases has not far from the same value.

But there is one other advance of fundamental importance which came with the study of the properties of gases ionized by X-rays. For up to this time the only type of ionization known was that observed in solution and here it is always some compound molecule like sodium chloride ( $\text{NaCl}$ ) which splits up spontaneously into a positively charged sodium ion and a negatively charged chlorine ion. But the ionization produced in gases by X-rays was of a wholly different sort, for it was observable in pure gases like nitrogen or oxygen, or even in monatomic gases like argon and helium. Plainly, then, the neutral atom even of a monatomic substance must possess minute electrical charges as constituents. Here we had the first direct evidence (1) that an atom is a complex structure, and (2) that electrical charges enter into its make-up. *With this discovery, due directly to the use of the new agency, X-rays, the atom as an ultimate, indivisible thing was gone, and the era of the study of the*

*constituents of the atom began.* And with astonishing rapidity during the past twenty-five years the properties of the subatomic world have been revealed.

Physicists began at once to seek diligently and to find at least partial answers to questions like these:

1. What are the masses of the constituents of the atoms torn asunder by X-rays and similar agencies?

2. What are the values of the charges carried by these constituents?

3. How many of these constituents are there?

4. How large are they, i.e., what volumes do they occupy?

5. What are their relations to the emission and absorption of light and heat waves, i.e., of electromagnetic radiation?

6. Do all atoms possess similar constituents? In other words, is there a primordial subatom out of which atoms are made?

The partial answer to the first of these questions came with the study of the electrical behavior of rarefied gases in so-called vacuum tubes.

This field had been entered and qualitatively explored with amazing insight as early as 1879 by Sir William Crookes, who in describing in that year some of his experiments said:

The phenomena in these exhausted tubes reveal to physical science a new world—a world where matter exists in a fourth state. . . . In studying this fourth state of matter we seem at length to have within our grasp and obedient to our control the little indivisible particles which with good warrant are supposed to constitute the physical basis of the universe.<sup>1</sup>

Further, by 1890 Sir Arthur Schuster<sup>1</sup> had gone a step farther and shown how the ratio of the charge to the mass  $\left[\frac{e}{m}\right]$  of these same hypothetical particles might be determined. Indeed he had experimentally evaluated this ratio, obtaining, however, a value very much too small, namely,  $1.1 \times 10^{-6}$  electromagnetic units.

But it was J. J. Thomson<sup>2</sup> who in 1897 first introduced a more reliable method of determining this ratio, namely, one which combines a measurement of the magnetic deflectability of a beam of cathode rays with the electrostatic deflectability of the same beam. The value which he obtained, namely,  $7 \times 10^6$  electromagnetic units, was nearly a thousand times the value of  $\frac{e}{m}$  for the hydrogen ion in solutions. Also since the approximate equality of  $ne$  in gases and solutions meant that  $e$  was at least of the same order in both, the only possible conclusion was that the negative ion which appears in discharges in exhausted tubes has a mass, i.e., an inertia, only one-thousandth of the mass of the lightest-known atom, namely, the atom of hydrogen. Later more accurate experiments have fixed the correct value of  $\frac{e}{m}$  for cathode rays at  $1.768 \times 10^7$  electromagnetic units.

Furthermore, J. J. Thomson and after him other experimenters showed that  $\frac{e}{m}$  for the negative carrier is always the same whatever be the nature of the residual gas in the discharge tube. This was an indication of an affirmative answer to the sixth question above—an

<sup>1</sup> *Proc. Roy. Soc.*, XL (1890), 526.

<sup>2</sup> *Phil. Mag.*, XLIV (1897), 298.

indication which was strengthened by Zeeman's discovery in 1897 of the splitting by a magnetic field of a single spectral line into two or three lines; for this, when worked out quantitatively, pointed to the existence *within* the atom of a negatively charged particle which had approximately the same value of  $\frac{e}{m}$ .

The study of  $\frac{e}{m}$  for the *positive* ions in exhausted tubes was first carried out quantitatively by Wien,<sup>1</sup> and was later most elaborately and most successfully dealt with by J. J. Thomson<sup>2</sup> and his pupils at the Cavendish Laboratory. The results of the work of all observers up to date seem to show quite conclusively that  $\frac{e}{m}$  for a positive ion in gases is never larger than its value for the hydrogen ion in electrolysis, and that it varies with different sorts of residual gases just as it is found to do in electrolysis.

In a word, then, the act of ionization in gases appears to consist in the detachment from a neutral atom of one or more negatively charged particles, called by Thomson corpuscles. The residuum of the atom is of course positively charged, and it always carries practically the whole mass of the original atom. The detached corpuscle must soon attach itself, in a gas at ordinary pressure, to a neutral atom, since otherwise we could not account for the fact that the mobilities and the diffusion coefficients of negative ions are usually of the same order of magnitude as those of the positive ions. It is because of this tendency of the parts of the dissociated atom to

<sup>1</sup> W. Wien, *Wied. Ann.*, LXV (1898), 440.

<sup>2</sup> *Rays of Positive Electricity*. London: Longmans, 1913.

form new attachments in gases at ordinary pressure that the inertias of these parts had to be worked out in the rarefied gases of exhausted tubes.

The foregoing conclusions as to the masses of the positive and negative constituents of atoms had all been reached before 1900, mostly by the workers in the Cavendish Laboratory, and subsequent investigation has not modified them in any essential particulars.

The history of the development of our present knowledge of the charges carried by the constituents will be detailed in the next chapters.

## CHAPTER III

### EARLY ATTEMPTS AT THE DIRECT DETERMINATION OF $e$

Although the methods sketched in the preceding chapters had been sufficient to show that the mean charges carried by ions in gases are the same or nearly the same as the mean charges carried by univalent ions in solution, in neither case had we any way of determining what the absolute value of that mean charge is, nor, indeed, had we any proof even that all the ions of a given kind, e.g., silver or hydrogen, carry the same charge. Of course, the absolute value of  $e$  could be found from the measured value of  $ne$  if only  $n$ , the number of molecules in 1 c.c. of gas under standard conditions, were known. But we had only rough guesses as to this number. These guesses varied tenfold, and none of them were based upon considerations of recognized accuracy or even validity.

#### I. TOWNSEND'S WORK ON $e$

The first attempt at a direct determination of  $e$  was published by Townsend in a paper read before the Cambridge Philosophical Society on February 8, 1897.<sup>1</sup> Townsend's method was one of much novelty and of no little ingenuity. It is also of great interest because it contains all the essential elements of some of the subsequent determinations.

<sup>1</sup> *Proceedings*, IX (1897), 244.



It had been known, even to Laplace and Lavoisier a hundred years before, that the hydrogen gas evolved when a metal dissolves in an acid carries with it an electrical charge. This "natural method" of obtaining a charge on a gas was scarcely studied at all, however, until after the impulse to the study of the electrical properties of gases had been given by the discovery in 1896 that electrical properties can be artificially imparted to gases by X-rays. Townsend's paper appeared within a year of that time. Enright<sup>1</sup> had indeed found that the hydrogen given off when iron is dissolving in sulphuric acid carries with it a positive charge, but Oliver Lodge<sup>2</sup> had urged that it was not the gas itself which carries the charge but merely the spray, for the frictional electrification of spray was a well-known phenomenon. Indeed, it has always been assumed that the gas molecules which rise from the electrodes in electrolysis are themselves neutral. Townsend, however, first showed that some of these molecules are charged, although there are indeed a million million neutral ones for every one carrying a charge. He found that both the oxygen and the hydrogen which appear at the opposite electrodes when sulphuric acid is electrolyzed are positively charged, while when the electrolyte is caustic potash both the oxygen and the hydrogen given off are negative. Townsend's electrolyzing currents were from 12 to 14 amperes. He got in this way many more ions per cubic centimeter than he could produce with X-rays, the total charge per cubic centimeter being as large as  $5 \times 10^{-3}$  electrostatic units.

<sup>1</sup> *Phil. Mag.*, XXIX (1890; 5th series), 56.

<sup>2</sup> *Ibid.*, p. 292; *Nature*, XXXVI, 412.



When these charged gases were bubbled through water they formed a cloud. This cloud could be completely removed by bubbling through concentrated sulphuric acid or any drying agent, but when the gas came out again into the atmosphere of the room it again condensed moisture and formed a stable cloud. Townsend says that "the process of forming the cloud in positive or negative oxygen by bubbling through water, and removing it again by bubbling through sulphuric acid, can be gone through without losing more than 20 or 25 per cent of the original charge on the gas." This means simply that the ions condense the water about them when there is an abundance of moisture in the air, but when the cloud is carried into a perfectly dry atmosphere, such as that existing in a bubble surrounded on all sides by concentrated sulphuric acid, the droplets of water evaporate and leave the charge on a molecule of air as it was at first. The 20 or 25 per cent loss of charge represents the fraction of the droplets with their charges which actually got into contact with and remained in the liquids through which the gas was being bubbled.

In order to find the charge on each ion, Townsend took the following five steps:

1. He assumed that in saturated water vapor each ion condensed moisture about it, so that the number of ions was the same as the number of droplets.

2. He determined with the aid of a quadrant electrometer the total electrical charge per cubic centimeter carried by the gas.

3. He found the total weight of the cloud by passing it through drying tubes and determining the increase in weight of these tubes.

4. He found the average weight of the water droplets constituting the cloud by observing their rate of fall under gravity and computing their mean radius with the aid of a purely theoretical law known as Stokes's Law.

5. He divided the weight of the cloud by the average weight of the droplets of water to obtain the number of droplets which, if assumption 1 is correct, was the number of ions, and he then divided the total charge per cubic centimeter in the gas by the number of ions to find the average charge carried by each ion, that is, to find  $e$ .

A brief description of the way in which these experiments were carried out is contained in Appendix B.

One of the interesting side results of this work was the observation that clouds from negative oxygen fall faster than those from positive oxygen, thus indicating that the negative ions in oxygen act more readily than do the positive ions as nuclei for the condensation of water vapor. This observation was made at about the same time in another way by C. T. R. Wilson,<sup>1</sup> also in the Cavendish Laboratory, and it has played a rather important rôle in subsequent work. Wilson's discovery was that when air saturated with water vapor is ionized by X-rays from radioactive substances and then cooled by a sudden expansion, a smaller expansion is required to make a cloud form about the negative than about the positive ions. Thus when the expansion increased the volume in a ratio between 1.25 and 1.3, only negative ions acted as nuclei for cloudy condensation, while with expansions greater than 1.3 both negatives and positives were brought down.

<sup>1</sup> *Proc. Camb. Phil. Soc.*, IX (1897), 333.

Townsend first obtained by the foregoing method, when he worked with positive oxygen,

$$e = 2.8 \times 10^{-10} \text{ electrostatic units,}$$

and when he worked with negative oxygen,

$$e = 3.1 \times 10^{-10} \text{ electrostatic units.}$$

In later experiments<sup>1</sup> he obtained 2.4 and 2.9, respectively, in place of the numbers given above, but in view of the unavoidable errors, he concluded that the two charges might be considered equal and approximately  $3 \times 10^{-10}$  electrostatic units. Thus he arrived at about the same value for  $e$  as that which was then current because of the kinetic theory estimates of  $n$ , the number of molecules in a cubic centimeter of a gas.

The weak points in this first attempt at a direct determination of  $e$  consisted in: (1) the assumption that the number of ions is the same as the number of drops; (2) the assumption of Stokes's Law of Fall which had never been tested experimentally, and which from a theoretical standpoint might be expected to be in error when the droplets were small enough; (3) the assumption that the droplets were all alike and fell at a uniform rate wholly uninfluenced by evaporation or other causes of change; (4) the assumption of no convection currents in the gas when the rate of fall of the cloud was being measured.

## II. SIR JOSEPH THOMSON'S WORK ON $e$

This first attempt to measure  $e$  was carried out in Professor J. J. Thomson's laboratory. The second attempt was made by Professor Thomson himself<sup>2</sup> by a method

<sup>1</sup> *Ibid.*, p. 345.

<sup>2</sup> *Phil. Mag.*, XLVI (1898), 528.

which resembled Townsend's very closely in all its essential particulars. Indeed, we may set down for Professor Thomson's experiment precisely the same five elements which are set down on p. 45 for Townsend's. The differences lay wholly in step 2, that is, in the way in which the electrical charge per cubic centimeter carried by the gas was determined, and in step 3, that is, in the way in which the total weight of the cloud was obtained. Thomson produced ions in the space *A* (Fig. 1) by an X-ray bulb which ran at a constant rate, and measured first the current which, under the influence of a very weak electromotive force *E*, flows through *A* between the surface of the water and the aluminum plate which closes the top of the vessel. Then if *n'* is the whole number of ions of one sign per cubic centimeter, *u* the velocity of the positive and *v* that of the negative ion under unit electric force, i.e., if *u* and *v* are the mobilities of the positive and negative ions, respectively, then the current *I* per unit area is evidently given by

$$I = n'e(u+v) E \dots \dots \dots (4)$$

*I* and *E* were easily measured in any experiment; *u+v* was already known from Rutherford's previous work, so that *n'e*, the charge of one sign per cubic centimeter of gas under the ionizing action of a constant source of X-rays, could be obtained at once from (4). This then simply replaces Townsend's method of obtaining the charge per cubic centimeter on the gas, and in principle the two methods are quite the same, the difference in experimental arrangements being due to the fact that Townsend's ions are of but one sign while Thomson's are of both signs.

Having thus obtained  $n'e$  of equation (4), Thomson had only to find  $n'$  and then solve for  $e$ . To obtain  $n'$  he proceeded exactly as Townsend had done in letting the ions condense droplets of water about them and weighing the cloud thus formed. But in order to form the cloud, Thomson utilized C. T. R. Wilson's discovery

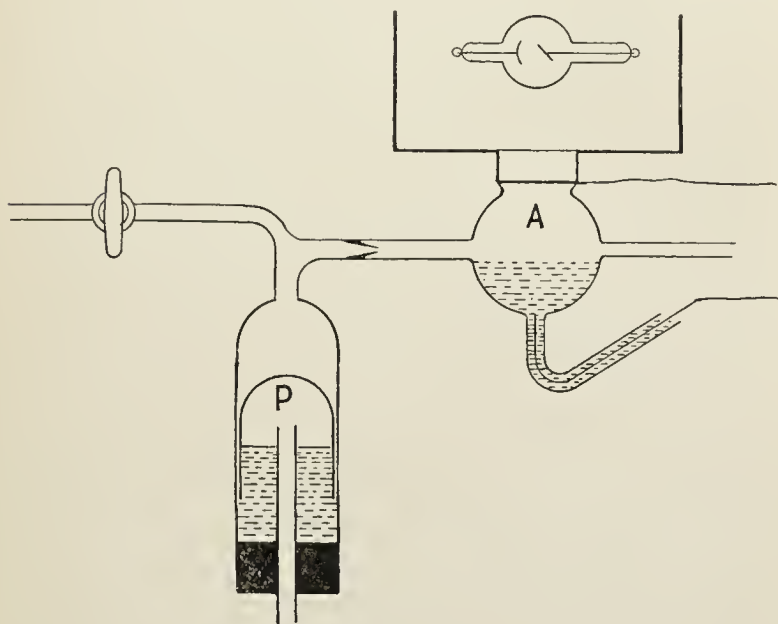


FIG. 1

just touched upon above, that a sudden expansion and consequent cooling of the air in  $A$  (Fig. 1) would cause the ions in  $A$  to act as nuclei for the formation of water droplets. To produce this expansion the piston  $P$  is suddenly pulled down so as to increase the volume of the space above it. A cloud is thus formed about the ions in  $A$ . Instead of measuring the weight of this cloud directly, as Townsend had done, Thomson computed it by a theoretical consideration of the amount of cooling

produced by the expansion and the known difference between the densities of saturated water vapor at the temperature of the room and the temperature resulting from the expansion. This method of obtaining the weight of the cloud was less direct and less reliable than that used by Townsend, but it was the only one available with Thomson's method of obtaining an ionized gas and of measuring the charge per cubic centimeter on that gas. The average size of the droplets was obtained precisely as in Townsend's work by applying Stokes's Law to the observed rate of fall of the top of the cloud in chamber A.

The careful consideration of Thomson's experiment shows that it contains the theoretical uncertainties involved in Townsend's work, while it adds some very considerable experimental uncertainties. The most serious of the theoretical uncertainties arise from (1) the assumption of Stokes's Law, and (2) the assumption that the number of ions is equal to the number of droplets. Both observers sought for some experimental justification for the second and most serious of these assumptions, but subsequent work by H. A. Wilson, by Quincke, and by myself has shown that clouds formed by C. T. R. Wilson's method consist in general of droplets some of which may carry one, some two, some ten, or almost any number of unit charges, and I have never been able, despite quite careful experimenting, to obtain conditions in which it was even approximately true that each droplet carried but a single unit charge. Quincke has recently published results from which he arrives at the same conclusion.<sup>1</sup>

<sup>1</sup> *Verh. der deutsch. phys. Ges.*, XVI (1914), 422.



Again, when we compare the *experimental* uncertainties in Townsend's and Thomson's methods, it is at once obvious that the assumption that the clouds are not evaporating while the rate of fall is being determined is even more serious in Thomson's experiment than in Townsend's, for the reason that in the former case the clouds are formed by a sudden expansion and a consequent fall in temperature, and it is certain that during the process of the return of the temperature to initial conditions the droplets must be evaporating. Furthermore, this sudden expansion makes the likelihood of the existence of convection currents, which would falsify the computations of the radius of the drop from the observed rate of fall, more serious in Thomson's work than in Townsend's. The results which Thomson attained in different experiments gave values ranging from  $5.5 \times 10^{-10}$  to  $8.4 \times 10^{-10}$ . He published as his final value  $6.5 \times 10^{-10}$ . In 1903, however,<sup>1</sup> he published some new work on  $e$  in which he had repeated the determination, using the radiation from radium in place of that from X-rays as his ionizing agent and obtained the result  $e = 3.4 \times 10^{-10}$ . He explained the difference by the assumption that in his preceding work the more active negative ions had monopolized the aqueous vapor available and that the positive ions had not been brought down with the cloud as he had before assumed was the case. He now used more sudden expansions than he had used before, and concluded that the assumption made in the earlier experiments that the number of ions was equal to the number of particles, although shown to be incorrect for the former case, was correct for these

<sup>1</sup> *Phil. Mag.*, V (1903; 6th series), 354.



second experiments. As a matter of fact, if he had obtained only half the ions in the first experiments and all of them in the second, his second result should have come out approximately one-half as great as the first, which it actually did. Although Thomson's experiment was an interesting and important modification of Townsend's, it can scarcely be said to have added greatly to the accuracy of our knowledge of  $e$ .

The next step in advance in the attempt at the determination of  $e$  was made in 1903 by H. A. Wilson,<sup>1</sup> also in the Cavendish Laboratory.

### III. H. A. WILSON'S METHOD

Wilson's modification of Thomson's work consisted in placing inside the chamber  $A$  two horizontal brass plates  $3\frac{1}{2}$  cm. in diameter and from 4 to 10 mm. apart and connecting to these plates the terminals of a 2,000-volt battery. He then formed a negative cloud by a sudden expansion of amount between 1.25 and 1.3, and observed first the rate of fall of the top surface of this cloud between the plates when no electrical field was on; then he repeated the expansion and observed the rate of fall of the cloud when the electrical field as well as gravity was driving the droplets downward. If  $mg$  represents the force of gravity acting on the droplets in the top surface of the cloud and  $mg+Fe$  the force of gravity plus the electrical force arising from the action of the field  $F$  on the charge  $e$ , and if  $v_1$  is the velocity of fall under the action of gravity alone, and  $v_2$  the velocity when both gravity and the electrical field are acting, then, if the ratio between the force acting and

<sup>1</sup> *Op. cit.*, p. 429.

the velocity produced is the same when the particle is charged as when it is uncharged, we have

$$\frac{mg}{mg+Fe} = \frac{v_1}{v_2} \dots \dots \dots (5)$$

Combining this with the Stokes's Law equation which runs

$$v_1 = \frac{2}{9} \frac{ga^2\sigma}{\eta} \dots \dots \dots (6)$$

in which  $a$  is the radius,  $\sigma$  the density,  $v_1$  the velocity of the drop under gravity  $g$ , and  $\eta$  is the viscosity of the air, and then eliminating  $m$  by means of

$$m = \frac{4}{3}\pi a^3\sigma \dots \dots \dots (7)$$

Wilson obtained after substituting for  $\eta$  and  $\sigma$  the appropriate values (not accurately known, it is true, for saturated air at the temperature existing immediately after the expansion),

$$e = 3.1 \times 10^{-9} \frac{g}{F}(v_2 - v_1)v_1^{\frac{1}{2}} \dots \dots \dots (8)$$

Wilson's method constitutes a real advance in that it eliminates the necessity of making the very awkward assumption that the number of droplets is equal to the number of negative ions, for since he observes only the rate of fall of the *top* of the cloud, and since the more heavily charged droplets will be driven down more rapidly by the field than the less heavily charged ones, his actual measurements would always be made upon *the least heavily charged droplets*. All of the other difficulties and assumptions contained in either Townsend's or Thomson's experiments inhere also in Wilson's, and in addition one fresh and rather serious assumption

is introduced, namely, that the clouds formed in successive expansions are identical as to size of droplets. For we wrote down the first equation of Wilson's method as though the  $v_1$  and  $v_2$  were measurements made upon the same droplet, when as a matter of fact the measurements are actually made on wholly different droplets. I have myself found the duplication of cloud conditions in successive expansions a very uncertain matter. Furthermore, Wilson's method assumes uniformity in the field between the plates, an assumption which might be quite wide of the truth.

Although the elimination of the assumption of equality of the number of droplets and the number of ions makes Wilson's determination of  $e$  more reliable as to method than its predecessors, the accuracy actually attained was not great, as can best be seen from his own final summary of results. He made eleven different determinations which varied from  $e = 2 \times 10^{-10}$  to  $e = 4.4 \times 10^{-10}$ . His eleven results are:

TABLE I

$e$	$e$
$2.3 \times 10^{-10}$	$3.8 \times 10^{-10}$
2.6 "	3.0 "
4.4 "	3.5 "
2.7 "	2.0 "
3.4 "	2.3 "
3.8 "	
Mean	$3.1 \times 10^{-10}$

In 1906, being dissatisfied with the variability of these results, the author repeated Wilson's experiment without obtaining any greater consistency than that which the latter had found. Indeed, the instability, distortion, and indefiniteness of the top surface of the cloud were some-

what disappointing, and the results were not considered worth publishing. Nevertheless, it was concluded from these observations that the accuracy might be improved by using radium instead of X-rays for the ionizing agent, by employing stronger electrical fields, and thus increasing the difference between  $v_1$  and  $v_2$ , which in Wilson's experiment had been quite small, and by observing the fall of the cloud through smaller distances and shorter times in order to reduce the error due to the evaporation of the cloud during the time of observation. Accordingly, a 4,000-volt storage battery was built and in the summer of 1908 Mr. Begeman and the author, using radium as the ionizing agent, again repeated the experiment and published some results which were somewhat more consistent than those reported by Wilson.<sup>1</sup> We gave as the mean of ten observations which varied from 3.66 to 4.37 the value  $e = 4.06 \times 10^{-10}$ . We stated at the time that although we had not eliminated altogether the error due to evaporation, we thought that we had rendered it relatively harmless, and that our final result, although considerably larger than either Wilson's or Thomson's (3.1 and 3.4, respectively), must be considered an approach at least toward the correct value.

#### IV. THE BALANCED-DROP METHOD

Feeling, however, that the amount of evaporation of the cloud was still a quite unknown quantity, I next endeavored to devise a way of eliminating it entirely. The plan now was to use an electrical field which was strong enough, not merely to increase or decrease slightly the speed of fall under gravity of the top surface of the

<sup>1</sup> *Phys. Rev.*, XXVI (1908), 198.

cloud, as had been done in all the preceding experiments, but also sufficiently strong to hold the top surface of the cloud stationary, so that the rate of its evaporation could be accurately observed and allowed for in the computations.

This attempt, while not successful in the form in which it had been planned, led to a modification of the cloud method which seemed at the time, and which has actually proved since, to be of far-reaching importance. *It made it for the first time possible to make all the measurements on individual droplets*, and thus not merely to eliminate ultimately all of the questionable assumptions and experimental uncertainties involved in the cloud method of determining  $e$ , but, more important still, it made it possible to examine the properties of individual isolated electrons and to determine whether different ions actually carry one and the same charge. That is to say, it now became possible to determine whether electricity in gases and solutions is actually built up out of electrical atoms, each of which has exactly the same value, or whether the electron which had first made its appearance in Faraday's experiments on solutions and then in Townsend's and Thomson's experiments on gases is after all only a *statistical mean* of charges which are themselves greatly divergent. This latter view had been strongly urged up to and even after the appearance of the work which is now under consideration. It will be given further discussion presently.

The first determination which was made upon the charges carried by individual droplets was carried out in the spring of 1909. A report of it was placed upon the program of the British Association meeting at Winni-

peg in August, 1909, as an additional paper, was printed in abstract in the *Physical Review* for December, 1909, and in full in the *Philosophical Magazine* for February, 1910, under the title "A New Modification of the Cloud Method of Determining the Elementary Electrical Charge and the Most Probable Value of That Charge."<sup>1</sup> The following extracts from that paper show clearly what was accomplished in this first determination of the charges carried by individual droplets.

THE BALANCING OF INDIVIDUAL CHARGED DROPS BY AN  
ELECTROSTATIC FIELD

My original plan for eliminating the evaporation error was to obtain, if possible, an electric field strong enough exactly to balance the force of gravity upon the cloud and then by means of a sliding contact to vary the strength of this field so as to hold the cloud balanced throughout its entire life. In this way it was thought that the whole evaporation-history of the cloud might be recorded, and that suitable allowances might then be made in the observations on the rate of fall to eliminate entirely the error due to evaporation. It was not found possible to balance the cloud, as had been originally planned, but it was found possible to do something much better: namely, to hold individual charged drops suspended by the field for periods varying from 30 to 60 seconds. I have never actually timed drops which lasted more than 45 seconds, although I have several times observed drops which in my judgment lasted considerably longer than this. The drops which it was found possible to balance by an electrical field always carried multiple charges, and the difficulty experienced in balancing such drops was less than had been anticipated.

The procedure is simply to form a cloud and throw on the field immediately thereafter. The drops which have charges of the same sign as that of the upper plate or too weak charges of the opposite sign rapidly fall, while those which are charged with too many multiples of the sign opposite to that of the upper plate are

<sup>1</sup> *Phil. Mag.*, XIX (1910), 209.



jerked up against gravity to this plate. The result is that after a lapse of 7 or 8 seconds the field of view has become quite clear save for a relatively small number of drops which have just the right ratio of charge to mass to be held suspended by the electric field. These appear as perfectly distinct bright points. I have on several occasions obtained but one single such "star" in the whole field and held it there for nearly a minute. For the most part, however, the observations recorded below were made with a considerable number of such points in view. Thin, flocculent clouds, the production of which seemed to be facilitated by keeping the water-jackets  $J_1$  and  $J_2$  (Fig. 2) a degree or two above the temperature of the room, were found to be particularly favorable to observations of this kind.

Furthermore, it was found possible so to vary the mass of a drop by varying the ionization, that drops carrying in some cases two, in some three, in some four, in some five, and in some six, multiples, could be held suspended by nearly the same field. The means of gradually varying the field which had been planned were therefore found to be unnecessary. If a given field would not hold any drops suspended it was varied by steps of 100 or 200 volts until drops were held stationary, or nearly stationary. When the P.D. was thrown off it was often possible to see different drops move down under gravity with greatly different speeds, thus showing that these drops had different masses and correspondingly different charges.

The life-history of these drops is as follows: If they are a little too heavy to be held quite stationary by the field they begin to move slowly down under gravity. Since, however, they slowly evaporate, their downward motion presently ceases, and they become stationary for a considerable period of time. Then the field gets the better of gravity and they move slowly upward. Toward the end of their life in the space between the plates, this upward motion becomes quite rapidly accelerated and they are drawn with considerable speed to the upper plate. This, taken in connection with the fact that their whole life between plates only 4 or 5 mm. apart is from 35 to 60 seconds, will make it obvious that during a very considerable fraction of this time their motion must be exceedingly slow. I have often held drops through a



period of from 10 to 15 seconds, during which it was impossible to see that they were moving at all. Shortly after an expansion I have seen drops which at first seemed stationary, but which then began to move slowly down in the direction of gravity, then become stationary again, then finally began to move slowly up. This is probably due to the fact that large multiply charged drops are not in equilibrium with smaller singly charged drops near them, and hence, instead of evaporating, actually grow for a time at the expense of their small neighbors. Be this as it may, however, it is by utilizing the experimental fact that there is a considerable period during which the drops are essentially stationary that it becomes possible to make measurements upon the rate of fall in which the error due to evaporation is wholly negligible in comparison with the other errors of the experiment. Furthermore, in making measurements of this kind the observer is just as likely to time a drop which has not quite reached its stationary point as one which has just passed through that point, so that the mean of a considerable number of observations would, even from a theoretical standpoint, be quite free from an error due to evaporation.

#### THE METHOD OF OBSERVATION

The observations on the rate of fall were made with a short-focus telescope  $T$  (see Fig. 2) placed about 2 feet away from the plates. In the eyepiece of this telescope were placed three equally spaced cross-hairs, the distance between those at the extremes corresponding to about one-third of the distance between the plates. A small section of the space between the plates was illuminated by a narrow beam from an arc light, the heat of the arc being absorbed by three water cells in series. The air between the plates was ionized by 200 mg. of radium, of activity 20,000, placed from 3 to 10 cm. away from the plates. A second or so after expansion the radium was removed, or screened off with a lead screen, and the field thrown on by hand by means of a double-throw switch. If drops were not found to be held suspended by the field, the P.D. was changed or the expansion varied until they were so held. The cross-hairs were set near the lower plate, and as soon as a stationary drop was found somewhere above the upper cross-hair, it was watched for a few seconds to make sure that it was not moving,

and then the field was thrown off and the plates short-circuited by means of the double-throw switch, so as to make sure that they retained no charge. The drop was then timed by means of an accurate stop watch as it passed across the three cross-hairs, one of the two hands of the watch being stopped at the instant of

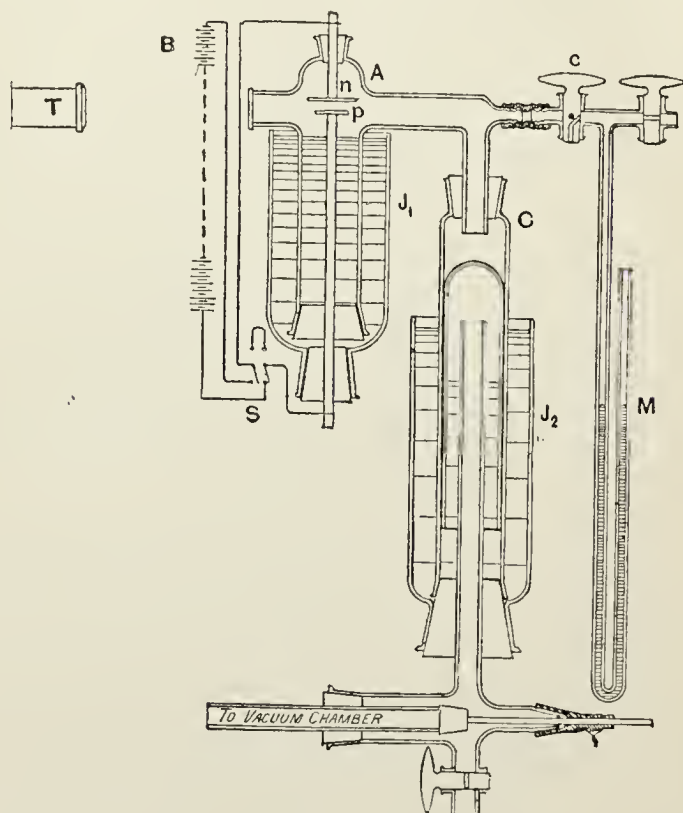


FIG. 2

passage across the middle cross-hair, the other at the instant of passage across the lower one. It will be seen that this method of observation furnishes a double check upon evaporation; for if the drop is stationary at first, it is not evaporating sufficiently to influence the reading of the rate of fall, and if it begins to evaporate appreciably before the reading is completed, the time required to pass through the second space should be greater than that required

to pass through the first space. It will be seen from the observations which follow that this was not, in general, the case.

It is an exceedingly interesting and instructive experiment to watch one of these drops start and stop, or even reverse its direction of motion, as the field is thrown off and on. I have often caught a drop which was just too light to remain stationary and moved it back and forth in this way four or five times between the same two cross-hairs, watching it first fall under gravity when the field was thrown off and then rise against gravity when the field was thrown on. The accuracy and certainty with which the instants of passage of the drops across the cross-hairs can be determined are precisely the same as that obtainable in timing the passage of a star across the cross-hairs of a transit instrument.

Furthermore, since the observations upon the quantities occurring in equation (4) [see (8) p. 55 of this volume] are all made upon the same drop, all uncertainties as to whether conditions can be exactly duplicated in the formation of successive clouds obviously disappear. There is no theoretical uncertainty whatever left in the method unless it be an uncertainty as to whether or not Stokes's Law applies to the rate of fall of these drops under gravity. The experimental uncertainties are reduced to the uncertainty in a time determination of from 3 to 5 seconds, when the object being timed is a single moving bright point. This means that when the time interval is say 5 seconds, as it is in some of the observations given below, the error which a practiced observer will make with an accurate stop watch in any particular observation will never exceed 2 parts in 50. The error in the mean of a considerable number of concordant observations will obviously be very much less than this.

Since in this form of observation the  $v_2$  of equation (5) [(8) of this volume] is zero, and since  $F$  is negative in sign, equation (5) reduces to the simple form:

$$z = 3.422 \times 10^{-9} \times \frac{g}{X} (v_1)^{\frac{2}{3}} \dots \dots \dots (6)^1$$

<sup>1</sup> I had changed the constant in Wilson's equation from 3.1 to 3.422 because of careful measurements on the temperature existing in the cloud chamber about 10 seconds after expansion and because of new measurements on the viscosity of the saturated air.

It will perhaps be of some interest to introduce two tables from this paper to show the exact nature of these

TABLE II

SERIES 1 (BALANCED POSITIVE  
WATER DROPS)

Distance between plates .545 cm.  
Measured distance of fall .155 cm.

Volts	Time 1 Space	Time 2 Spaces
2,285.....	2.4 sec.	4.8 sec.
2,285.....	2.4	4.8
2,275.....	2.4	4.8
2,325.....	2.4	4.8
2,325.....	2.6	4.8
2,325.....	2.2	4.8
2,365.....	2.4	4.8
2,312.....	2.4	4.8

Mean time for .155 cm.=4.8 sec.

$$e_3 = 3.422 \times 10^{-9} \times \frac{980.3}{14.14} \times \left( \frac{.155}{4.8} \right)^{\frac{2}{3}}$$

$$= 13.77 \times 10^{-10}$$

Therefore  $e = 13.85 \times 10^{-10} \div 3$   
 $= 4.59 \times 10^{-10}.$

SERIES 2 (BALANCED POSITIVE  
WATER DROPS)

Distance between plates .545 cm.  
Measured distance of fall .155 cm.

Volts	Time 1 Space	Time 2 Spaces
2,365.....	1.8 sec.	4.0 sec.
2,365.....	1.8	4.0
2,365.....	2.2	3.8
2,365.....	1.8	4.0
2,395.....	2.0	4.0
2,395.....	2.0	4.0
2,395.....	2.0	3.8
2,365.....	1.8	4.0
2,365.....	1.8	4.0
2,365.....	1.8	4.0
2,374.....	1.90	3.96

Mean time for .155 cm.=3.91 sec.

$$e_4 = 3.422 \times 10^{-9} \times \frac{980.3}{14.52} \times \left( \frac{.155}{3.91} \right)^{\frac{2}{3}}$$

$$= 18.25 \times 10^{-10}$$

Therefore  $e = 18.25 \div 4$   
 $= 4.56 \times 10^{-10}.$

TABLE III

Series	Charge	Value of $e$	Weight Assigned
1.....	3e	4.59	7
2.....	4e	4.56	7
3.....	2e	4.64	6
4.....	5e	4.83	4
5.....	2e	4.87	1
6.....	6e	4.69	3

Simple mean  $e = 4.70 \times 10^{-10}$

Weighted mean  $e = 4.65 \times 10^{-10}$

earliest measurements on the charges carried by individual particles.

In connection with these experiments I chanced to observe a phenomenon which interested me very much at the time and suggested quite new possibilities. While working with these "balanced drops" I noticed on several occasions on which I had failed to screen off the rays from the radium that now and then one of them would suddenly change its charge and begin to move up or down in the field, evidently because it had captured in the one case a positive, in the other a negative, ion. This opened up the possibility of measuring with certainty, not merely the charges on individual droplets as I had been doing, but the charge carried by a single atmospheric ion. *For by taking two speed measurements on the same drop, one before and one after it had caught an ion, I could obviously eliminate entirely the properties of the drop and of the medium and deal with a quantity which was proportional merely to the charge on the captured ion itself.*

Accordingly, in the fall of 1909 there was started the series of experiments described in the succeeding chapter.

The problem had already been so nearly solved by the work with the water droplets that there seemed no possibility of failure. It was only necessary to get a charged droplet entirely free from evaporation into the space between the plates of a horizontal air condenser and then, by alternately throwing on and off an electrical field, to keep this droplet pacing its beat up and down between the plates until it could catch an atmospheric ion in just the way I had already seen the water droplets do. The change in the speed in the field would then be exactly proportional to the charge on the ion captured.

## CHAPTER IV

### GENERAL PROOF OF THE ATOMIC NATURE OF ELECTRICITY

Although the "balanced-droplet method" just described had eliminated the chief sources of uncertainty which inhered in preceding work on  $e$  and had made it possible to assert with much confidence that the unit charge was a real physical entity and not merely a "statistical mean," it was yet very far from an exact method of studying the properties of gaseous ions. The sources of error or uncertainty which still inhered in it arose from (1) the lack of stagnancy in the air through which the drop moved; (2) the lack of perfect uniformity of the electrical field used; (3) the gradual evaporation of the drops, rendering it impossible to hold a given drop under observation for more than a minute or to time a drop as it fell under gravity alone through a period of more than five or six seconds; and (4) the assumption of the validity of Stokes's Law.

The method which was devised to replace it was not only entirely free from all of these limitations, but it constituted an entirely new way of studying ionization and one which at once yielded important results in a considerable number of directions. This chapter deals with some of these by-products of the determination of  $e$  which are of even more fundamental interest and importance than the mere discovery of the exact size of the electron.



# I. ISOLATION OF INDIVIDUAL IONS AND MEASUREMENT OF THEIR RELATIVE CHARGES

In order to compare the charges on different ions, the procedure adopted was to blow with an ordinary commercial atomizer an oil spray into the chamber *C* (Fig. 3).

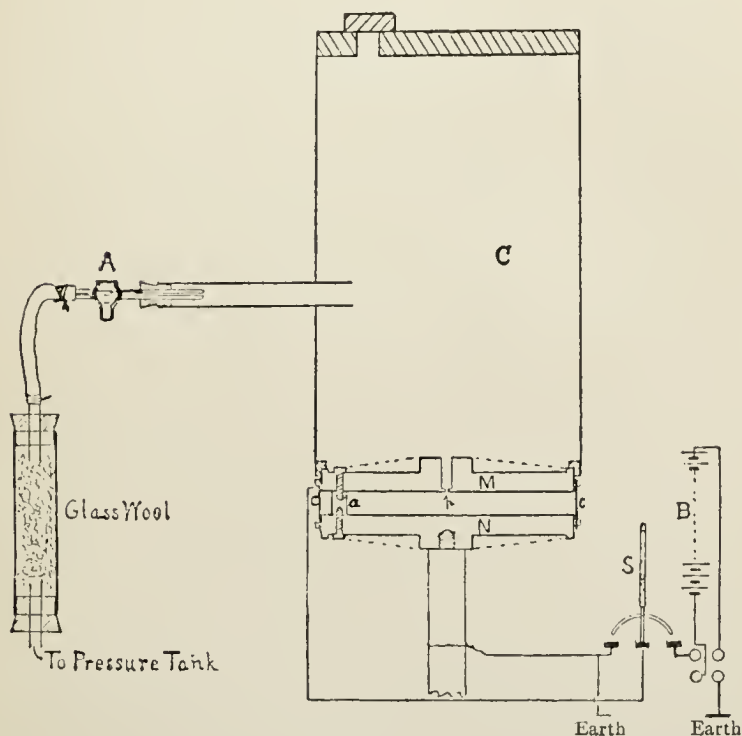


FIG. 3

The air with which this spray was blown was first rendered dust-free by passage through a tube containing glass wool. The minute droplets of oil constituting the spray, most of them having a radius of the order of a one-thousandth of a millimeter, slowly fell in the chamber *C*, and occasionally one of them would find its way



through the minute pinhole  $p$  in the middle of the circular brass plate  $M$ , 22 cm. in diameter, which formed one of the plates of the air condenser. The other plate,  $N$ , was held 16 mm. beneath it by three ebonite posts  $a$ . By means of the switch  $S$  these plates could be charged, the one positively and the other negatively, by making them the terminals of a 10,000-volt storage battery  $B$ , while throwing the switch the other way (to the left) short-circuited them and reduced the field between them to zero. The oil droplets which entered at  $p$  were illuminated by a powerful beam of light which passed through diametrically opposite windows in the encircling ebonite strip  $c$ . As viewed through a third window in  $c$  on the side toward the reader, it appeared as a bright star on a black background. These droplets which entered  $p$  were found in general to have been strongly charged by the frictional process involved in blowing the spray, so that when the field was thrown on in the proper direction they would be pulled up toward  $M$ . Just before the drop under observation could strike  $M$  the plates would be short-circuited and the drop allowed to fall under gravity until it was close to  $N$ , when the direction of motion would be again reversed by throwing on the field. In this way the drop would be kept traveling back and forth between the plates. The first time the experiment was tried an ion was caught within a few minutes, and the fact of its capture was signaled to the observer by the change in the speed with which it moved up when the field was on. The significance of the experiment can best be appreciated by examination of the complete record of one of the early experiments when the timing was done merely with a stop watch.

The column headed  $t_g$  gives the successive times which the droplet required to fall between two fixed cross-hairs in the observing telescope whose distance apart corresponded in this case to an actual distance of fall of .5222 cm. It will be seen that these numbers are all the same within the limits of error of a stop-watch measurement. The column marked  $t_F$  gives the successive times

TABLE IV

$t_g$	$t_F$
13.6	12.5
13.8	12.4
13.4	21.8
13.4	34.8
13.6	84.5
13.6	85.5
13.7	34.6
13.5	34.8
13.5	16.0
13.8	34.8
13.7	34.6
13.8	21.9
13.6	
13.5	
13.4	
13.8	
13.4	

Mean 13.595

which the droplet required to rise under the influence of the electrical field produced by applying in this case 5,051 volts of potential difference to the plates  $M$  and  $N$ . It will be seen that after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. The next time recorded under  $t_F$ , namely, 34.8, indicates that another negative ion had been caught. The next time, 84.5, indicates the capture

of still another negative ion. This charge was held for two trips, when the speed changed back again to 34.6, showing that a positive ion had now been caught which carried precisely the same charge as the negative ion which before caused the inverse change in time, i.e., that from 34.8 to 84.5.

In order to obtain some of the most important consequences of this and other similar experiments we need make no assumption further than this, that the velocity with which the drop moves is proportional to the force acting upon it and is independent of the electrical charge which it carries. Fortunately this assumption can be put to very delicate experimental test, as will presently be shown, but introducing it for the time being as a mere assumption, as Townsend, Thomson, and Wilson had done before, we get

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \text{ or } e_n = \frac{mg}{Fv_1}(v_1 + v_2) \dots\dots\dots (9)$$

The negative sign is used in the denominator because  $v_2$  will for convenience be taken as positive when the drop is going up in the direction of  $F$ , while  $v_1$  will be taken as positive when it is going down in the direction of  $g$ .  $e_n$  denotes the charge on the drop, and must not be confused with the charge on an ion. If now by the capture of an ion the drop changes its charge from  $e_n$  to  $e_{n'}$ , then the value of the captured charge  $e_i$  is

$$e_i = e_{n'} - e_n = \frac{mg}{Fv_1}(v'_2 - v_2) \dots\dots\dots (10)$$

and since  $\frac{mg}{Fv_1}$  is a constant for this drop, any charge which it may capture will always be proportional to

$(v' - v')$ , that is, to the change produced in the velocity in the field  $F$  by the captured ion. The successive values of  $v_2$  and of  $(v_2 - v_2)$ , these latter being obtained by subtracting successive values of the velocities given under  $v_2$ , are shown in Table V.

TABLE V

$v_2$	$(v'_1 - v_2)$
$\frac{.5222}{12.45} = .04196$	} $.01806 \div 2 = .00903$
$\frac{.5222}{21.5} = .02390$	
$\frac{.5222}{34.7} = .01505$	} $.00885 \div 1 = .00885$
$\frac{.5222}{85.0} = .006144$	
$\frac{.5222}{34.7} = .01505$	} $.00891 \div 1 = .00891$
$\frac{.5222}{16.0} = .03264$	
$\frac{.5222}{34.7} = .01505$	} $.00891 \div 1 = .00891$
$\frac{.5222}{21.85} = .02390$	
	} $.01759 \div 2 = .00880$
	} $.01759 \div 2 = .00880$
	} $.00891 \div 1 = .00891$

It will be seen from the last column that within the limits of error of a stop-watch measurement, all the charges captured have exactly the same value save in three cases. In all of these three the captured charges were just twice as large as those appearing in the other changes. Relationships of exactly this sort have been found to hold absolutely without exception, no matter in what gas the drops have been suspended or what sort of droplets were used upon which to catch the ions. In

many cases a given drop has been held under observation for five or six hours at a time and has been seen to catch not eight or ten ions, as in the experiment above, but hundreds of them. Indeed, I have observed, all told, the capture of many thousands of ions in this way, and in no case have I ever found one the charge of which, when tested as above, did not have either exactly the value of the smallest charge ever captured or else a very small multiple of that value. *Here, then, is direct, unimpeachable proof that the electron is not a "statistical mean," but that rather the electrical charges found on ions all have either exactly the same value or else small exact multiples of that value.*

## II. PROOF THAT ALL STATIC CHARGES BOTH ON CONDUCTORS AND INSULATORS ARE BUILT UP OF ELECTRONS

The foregoing experiment leads, however, to results of much more fundamental importance than that mentioned in the preceding section. The charge which the droplet had when it first came under observation had been acquired, not by the capture of ions from the air, but by the ordinary frictional process involved in blowing the spray. If then ordinary static charges are built up of electrons, this charge should be found to be an exact multiple of the ionic charge which had been found from the most reliable measurement shown in Table V to be proportional to the velocity .00891. This initial charge  $e_n$  on the drop is seen from equations (9) and (10) to bear the same relation to  $(v_1 + v_2)$  which the ionic charge  $e'_n - e_n$  bears to  $(v'_2 - v_2)$ . Now,  $v_1 = .5222 / 13.595 = .03842$ , hence  $v_1 + v_2 = .03842 + .04196 = .08038$ . Dividing this by 9 we obtain .008931, which is within about

one-fifth of 1 per cent of the value found in the last column of Table V as the smallest charge carried by an ion. *Our experiment has then given us for the first time a means of comparing a frictional charge with the ionic charge, and the frictional charge has in this instance been found to contain exactly 9 electrons.* A more exact means of making this comparison will be given presently, but suffice it to say here that experiments like the foregoing have now been tried on thousands of drops in different media, some of the drops being made of non-conductors like oil, some of semi-conductors like glycerin, some of excellent metallic conductors like mercury. In every case, without a single exception, the initial charge placed upon the drop by the frictional process, and all of the dozen or more charges which have resulted from the capture by the drop of a larger or smaller number of ions, have been found to be exact multiples of the smallest charge caught from the air. Some of these drops have started with no charge at all, and one, two, three, four, five, and six elementary charges or electrons have been picked up. Others have started with seven or eight units, others with twenty, others with fifty, others with a hundred, others with a hundred and fifty elementary units, and have picked up in each case a dozen or two of elementary charges on either side of the starting-point, so that, in all, drops containing every possible number of electrons between one and one hundred and fifty have been observed and the number of electrons which each drop carried has been accurately counted by the method described. When the number is less than fifty there is not a whit more uncertainty about this count than there is in counting one's own fingers and toes. It



is not found possible to determine with certainty the number of electrons in a charge containing more than one hundred or two hundred of them, for the simple reason that the method of measurement used fails to detect the difference between 200 and 201, that is, we cannot measure  $v'_2 - v_2$  with an accuracy greater than one-half of 1 per cent. But it is quite inconceivable that large charges such as are dealt with in commercial applications of electricity can be built up in an essentially different way from that in which the small charges whose electrons we are able to count are found to be. Furthermore, since it has been definitely proved that an electrical current is nothing but the motion of an electrical charge over or through a conductor, it is evident that the experiments under consideration furnish not only the most direct and convincing of evidence that all electrical charges are built up out of these very units which we have been dealing with as individuals in these experiments, but that all electrical currents consist merely in the transport of these electrons through the conducting bodies.

In order to show the beauty and precision with which these multiple relationships stand out in all experiments of this kind, a table corresponding to much more precise measurements than those given heretofore is here introduced (Table VI). The time of fall and rise shown in the first and second columns were taken with a Hipp chronoscope reading to one-thousandth of a second. The third column gives the reciprocals of these times. These are used in place of the velocities  $v_2$  in the field, since distance of fall and rise is always the same. The fourth column gives the successive changes in speed due



to the capture of ions. These also are expressed merely as time reciprocals. For reasons which will be explained in the next section, each one of these changes may correspond to the capture of not merely one but of several distinct ions. The numbers in the fifth column represent

TABLE VI

$t_g$ Sec.	$t_F$ Sec.	$\frac{1}{t_F}$	$\left(\frac{1}{t_F} - \frac{1}{t_g}\right)$	$n'$	$\frac{1}{n'} \left(\frac{1}{t_F} - \frac{1}{t_g}\right)$	$\left(\frac{1}{t_g} + \frac{1}{t_F}\right)$	$n$	$\frac{1}{n} \left(\frac{1}{t_g} + \frac{1}{t_F}\right)$
11.848	80.708	.01236	.03234	6	.005390	.09655	18	.005366
11.890	22.366							
11.908	22.390	.04470	.03751	7	.005358	.12887	24	.005371
11.904	22.368							
11.882	140.565	.007192	.005348	1	.005348	.09138	17	.005375
11.906	79.600	.01254						
11.838	34.748		.01616	3	.005387	.09673	18	.005374
11.816	34.762	.02870						
11.776	34.846					.11289	21	.005376
11.840	29.286							
11.904	29.236	.03414	.026872	5	.005375	.11833	22	.005379
11.870	137.308	.007268						
11.952	34.638	.02884	.021572	4	.005393	.09146	17	.005380
11.860								
11.846	22.104		.01623	3	.005410	.11303	21	.005382
11.912	22.268	.04507						
11.910	500.1	.002000	.04307	8	.005384	.12926	24	.005386
11.918	19.704	.05079						
11.870	19.668		.04879	9	.005421	.08619	16	.005387
11.888	77.630	.03794						
11.894	77.806	.01285	.03794	7	.005420	.13498	25	.005399
11.878	42.302	.02364						
11.880			Means		.005386			.005384

Duration of exp. = 45 min.  
 Plate distance = 16 mm.  
 Fall distance = 10.21 mm.  
 Initial volts = 5,088.8  
 Final volts = 5,081.2

Pressure = 75.62 cm.  
 Oil density = 9190  
 Air viscosity =  $1.824 \times 10^{-7}$   
 Radius ( $a$ ) = .000276 cm.  
 $\frac{l}{a}$  = .034

Temperature = 22.82° C.  
 Speed of fall = 08584 cm./sec.  
 $e = 4.991 \times 10^{-10}$

simply the small integer by which it is found that the numbers in the fourth column must be divided in order to obtain the numbers in the sixth column. These will be seen to be exactly alike within the limits of error of the experiment. The mean value at the bottom of the sixth column represents, then, the smallest charge ever caught

from the air, that is, it is the elementary *ionic* charge. The seventh column gives the successive values of  $v_1 + v_2$  expressed as reciprocal times. These numbers, then, represent the successive values of the *total* charge carried by the droplet. The eighth column gives the integers by which the numbers in the seventh column must be divided to obtain the numbers in the last column. These also will be seen to be invariable. The mean at the bottom of the last column represents, then, *the electrical unit out of which the frictional charge on the droplet was built up, and it is seen to be identical with the ionic charge represented by the number at the bottom of the sixth column.*

It may be of interest to introduce one further table (Table VII) arranged in a slightly different way to show

TABLE VII

$n$	$4.917 \times n$	Observed Charge	$n$	$4.917 \times n$	Observed Charge
1.....	4.917	.....	10.....	49.17	49.41
2.....	9.834	.....	11.....	54.09	53.91
3.....	14.75	.....	12.....	59.00	59.12
4.....	19.66	19.66	13.....	63.92	63.68
5.....	24.59	24.60	14.....	68.84	68.65
6.....	29.50	29.62	15.....	73.75	.....
7.....	34.42	34.47	16.....	78.67	78.34
8.....	39.34	39.38	17.....	83.59	83.22
9.....	44.25	44.42	18.....	88.51	.....

how infallibly the atomic structure of electricity follows from experiments like those under consideration.

In this table 4.917 is merely a number obtained precisely as above from the change in speed due to the capture of ions and one which is proportional in this experiment to the ionic charge. The column headed  $4.917 \times n$  contains simply the whole series of exact mul-

tiples of this number from 1 to 18. The column headed "Observed Charge" gives the successive observed values of  $(v_1 + v_2)$ . It will be seen that during the time of observation, about four hours, this drop carried all possible multiples of the elementary charge from 4 to 18, save only 15. *No more exact or more consistent multiple relationship is found in the data which chemists have amassed on the combining powers of the elements and on which the atomic theory of matter rests than is found in the foregoing numbers.*

Such tables as these—and scores of them could be given—place beyond all question the view that an electrical charge wherever it is found, whether on an insulator or a conductor, whether in electrolytes or in metals, has a definite granular structure, that it consists of an exact number of specks of electricity (electrons) all exactly alike, which in static phenomena are scattered over the surface of the charged body and in current phenomena are drifting along the conductor. Instead of giving up, as Maxwell thought we should some day do, the "provisional hypothesis of molecular charges," we find ourselves obliged to make all our interpretations of electrical phenomena, *metallic as well as electrolytic*, in terms of it.

### III. MECHANISM OF CHANGE OF CHARGE OF A DROP

All of the changes of charge shown in Table IV were spontaneous changes, and it has been assumed that all of these changes were produced by the capture of ions from the air. When a negative drop suddenly increases its speed in the field, that is, takes on a larger charge of its own kind than it has been carrying, there seems to be no other conceivable way in which the change can be

produced. But when the charge suddenly *decreases* there is no a priori reason for thinking that the change may not be due as well to the direct loss of a portion of the charge as to the neutralization of this same amount of electricity by the capture of a charge of opposite sign. That, however, the changes do actually occur, when no X-rays or radioactive rays are passing between the plates, only by the capture of ions from the air, was rendered probable by the fact that drops not too heavily charged showed the same tendency on the whole to increase as to decrease in charge. This should not have been the case if there were two causes tending to decrease the charge, namely, direct loss and the capture of opposite ions, as against one tending to increase it, namely, capture of like ions. The matter was very convincingly settled, however, by making observations when the gas pressures were as low as 2 or 3 mm. of mercury. Since the number of ions present in a gas is in general directly proportional to the pressure, spontaneous changes in charge should almost never occur at these low pressures; in fact, it was found that drops could be held for hours at a time without changing. The frequency with which the changes occur decreases regularly with the pressure, as it should if the changes are due to the capture of ions. For the number of ions formed by a given ionizing agent must vary directly as the pressure.

Again, the changes do not, in general, occur when the electrical field is on, for then the ions are driven instantly to the plates as soon as formed, at a speed of, say, 10,000 cm. per second, and so do not have any opportunity to accumulate in the space between them. When the field is off, however, they do so accumulate, until, in

ordinary air, they reach the number of, say, 20,000 per cubic centimeter. These ions, being endowed with the kinetic energy of agitation characteristic of the temperature, wander rapidly through the gas and become a part of the drop as soon as they impinge upon it. It was thus that all the changes recorded in Table IV took place.

It is possible, however, so to control the changes as to place electrons of just such sign as one wishes, and of just such number as one wishes, within limits, upon a given drop. If, for example, it is desired to place a positive electron upon a given drop the latter is held with the aid of the field fairly close to the negative plate, say the upper plate; then an ionizing agent—X-rays or radium—is arranged to produce uniform ionization in the gas between the plates. Since now all the positive ions move up while the negatives move down, the drop is in a shower of positive ions, and if the ionization is intense enough the drop is sure to be hit. In this way a positive charge of almost any desired strength may be placed upon the drop.

Similarly, in order to throw a negative ion or ions upon the drop it is held by the field close to the lower, i.e., to the positive, plate in a shower of negative ions produced by the X-rays. It was in this way that most of the changes shown in Table VI were brought about. This accounts for the fact that they correspond in some instances to the capture of as many as six electrons.

When X-rays are allowed to fall directly upon the drop itself the change in charge may occur, not merely because of the capture of ions, but also because the rays eject beta particles, i.e., negative electrons, from the molecules of the drop. That changes in charge were

actually produced in this way in our experiments was proved conclusively in 1910 by the fact that when the pressure was reduced to a very low value and X-rays were allowed to pass through the air containing the drop, the latter would change readily in the direction of increasing positive or decreasing negative charge, but it could almost never be made to change in the opposite direction. This is because at these low pressures the rays can find very few gas molecules to ionize, while they detach negative electrons from the drop as easily as at atmospheric pressure. *This experiment proved directly that the charge carried by an ion in gases is the same as the charge on the beta or cathode-ray particle.*

When it was desired to avoid the direct loss of negative electrons by the drop, we arranged lead screens so that the drop itself would not be illuminated by the rays, although the gas underneath it was ionized by them.<sup>1</sup>

#### IV. DIRECT OBSERVATION OF THE KINETIC ENERGY OF AGITATION OF A MOLECULE

I have already remarked that when a drop carries but a small number of electrons it appears to catch ions of its own sign as rapidly as those of opposite signs—a result which seems strange at first, since the ions of opposite sign must be attracted, while those of like sign must be repelled. Whence, then, does the ion obtain the energy which enables it to push itself up against this electrostatic repulsion and attach itself to a drop already strongly charged with its own kind of electricity? It cannot obtain it from the field, since the phenomenon of capture occurs when the field is not on. It cannot

<sup>1</sup> See *Phil. Mag.*, XXI (1911), 757.



obtain it from any explosive process which frees the ion from the molecule at the instant of ionization, since in this case, too, ions would be caught as well, or nearly as well, when the field is on as when it is off. Here, then, is an absolutely direct proof that the ion must be endowed with a kinetic energy of agitation which is sufficient to push it up to the surface of the drop against the electrostatic repulsion of the charge on the drop.

This energy may easily be computed as follows: Let us take a drop, such as was used in one of these experiments, of radius .000197 cm. The potential at the surface of a charged sphere can be shown to be the charge divided by the radius. The value of the elementary electrical charge obtained from the best observations of this type, is  $4.774 \times 10^{-10}$  absolute electrostatic units. Hence the energy required to drive an ion carrying the elementary charge  $e$  up to the surface of a charged sphere of radius  $r$ , carrying 16 elementary charges, is

$$\frac{16e^2}{r} = \frac{16 \times (4.774 \times 10^{-10})^2}{.000197} = 1.95 \times 10^{-14} \text{ ergs}$$

Now, the kinetic energy of agitation of a molecule as deduced from the value of  $e$  herewith obtained, and the kinetic theory equation,  $p = \frac{1}{3}nm\bar{c}^2$ , is  $5.75 \times 10^{-14}$  ergs. According to the Maxwell-Boltzmann Law of the partition of energy, which certainly holds in gases, this should also be the kinetic energy of agitation of an ion. It will be seen that the value of this energy is approximately three times that required to push a single ion up to the surface of the drop in question. Hence the electrostatic forces due to 16 electrons on the drop are too weak to exert much influence upon the motion of an approaching



ion. But if it were possible to load up a drop with negative electricity until the potential energy of its charge were about three times as great as that computed above for this drop, then the phenomenon here observed of the catching of new negative ions by such a negatively charged drop should not take place, save in the exceptional case in which an ion might acquire an energy of agitation considerably larger than the mean value. Now, as a matter of fact, it was regularly observed that the heavily charged drops had a very much smaller tendency to pick up new negative ions than the more lightly charged drops, and, in one instance, we watched for four hours another negatively charged drop of radius .000658 cm., which carried charges varying from 126 to 150 elementary units, and which therefore had a potential energy of charge (computed as above on the assumption of uniform distribution) varying from  $4.6 \times 10^{-14}$  to  $5.47 \times 10^{-14}$ . In all that time this drop picked up but one single negative ion when the field was off, and that despite the fact that the ionization was several times more intense than in the case of the drop of Table I. Positive ions too were being caught at almost every trip down under gravity. (The strong negative charge on the drop was maintained by forcing on negative ions by the field as explained above.)

#### V. POSITIVE AND NEGATIVE ELECTRONS EXACTLY EQUAL

The idea has at various times been put forth in connection with attempts to explain chemical and cohesive forces from the standpoint of electrostatic attractions that the positive and negative charges in a so-called neutral atom may not after all be exactly equal, in other

words, that there is really no such thing as an entirely neutral atom or molecule. As a matter of fact, it is difficult to find decisive tests of this hypothesis. The present experiments, however, make possible the following sort of test. I loaded a given drop first with negative electrons and took ten or twelve observations of rise and fall, then with the aid of X-rays, by the method indicated in the last section, I reversed the sign of the charge on the drop and took a corresponding number of observations of rise and fall, and so continued observing first the value of the negative electron and then that of the positive. Table VIII shows a set of such observations taken in air with a view to subjecting this point to as rigorous a test as possible. Similar, though not quite so elaborate, observations have been made in hydrogen with the same result. The table shows in the first column the sign of the charge; in the second the successive values of the time of fall under gravity; in the third the successive times of rise in the field  $F$ ; in the fourth the number of electrons carried by the drop for each value of  $t_F$ ; and in the fifth the number, characteristic of this drop, which is proportional to the charge of one electron. This number is obtained precisely as in the two preceding tables by finding the greatest common divisor of the successive values of  $(v_1 + v_2)$  and then multiplying this by an arbitrary constant which has nothing to do with the present experiment and hence need not concern us here (see chap. v).

It will be seen that though the times of fall and of rise, even when the same number of electrons is carried by the drop, change a trifle because of a very slight evaporation and also because of the fall in the potential

TABLE VIII

Sign of Drop	$t_g$ Sec.	$t_F$ Sec.	$n$	$e$
-	63.118		8	$e_1=6.713$
	63.050			
	63.186	41.728		
	63.332	41.590		
	62.328		11	
	62.728	25.740		
	62.926	25.798		
	62.900	25.510		
	63.214	25.806		
	Mean=62.976			
+	63.538	22.694	12	$e_1=6.692$
	63.244	22.830		
	63.114	25.870	11	
	63.242	25.876		
	63.362	25.484		
	63.136	10.830	22	
	63.226	10.682		
	63.764	10.756		
	63.280	10.778		
	63.530	10.672		
	63.268	10.646		
	Mean=63.325			
+	63.642		6	$e_1=6.702$
	63.020	71.664		
	62.820	71.248		
	63.514	52.668	7	
	63.312	52.800		
	63.776	52.496		
	63.300	52.860		
	63.156	71.708	6	
	63.126			
	Mean=63.407			

TABLE VIII—*Continued*

Sign of Drop	$t_g$ Sec.	$t_F$ Sec.	$n$	$e$
—	63.228	42.006	8	$e_1 = 6.686$
	63.294	41.920		
	63.184	42.108		
	63.260	53.210	7	
	63.478	52.922		
	63.074	53.034		
	63.306	53.438		
	63.414	12.888	19	
	63.450	12.812		
	63.446	12.748		
	63.556	12.824		
	Mean = 63.335			

Duration of experiment 1 hr. 40 min.

 Mean  $e_+ = 6.697$ 

Initial volts = 1723.5

 Mean  $e_- = 6.700$ 

Final volts = 1702.1

Pressure = 53.48 cm.

of the battery, yet the mean value of the positive electron, namely, 6.697, agrees with the mean value of the negative electron, namely, 6.700, to within less than 1 part in 2,000. Since this is about the limit of the experimental error (the probable error by least squares is 1 part in 1,500), *we may with certainty conclude that there are no differences of more than this amount between the values of the positive and negative electrons.* This is the best evidence I am aware of for the exact neutrality of the ordinary molecules of gases. Such neutrality, if it is actually exact, would seem to preclude the possibility of explaining gravitation as a result of electrostatic forces of any kind. The electromagnetic effect of moving charges might, however, still be called upon for this purpose.

VI. RESISTANCE OF MEDIUM TO MOTION OF DROP THROUGH  
IT THE SAME WHEN DROP IS CHARGED AS WHEN  
UNCHARGED

A second and equally important conclusion can be drawn from Table VIII. It will be seen from the column headed " $n$ " that during the whole of the time corresponding to the observations in the third group from the top the drop carried either 6 or 7 electrons, while, during the last half of the time corresponding to the observations in the second group from the top, it carried three times as many, namely, 22 electrons. Yet the mean times of fall under gravity in the two groups agree to within about one part in one thousand. The time of fall corresponding to the heavier charge happens in this case to be the smaller of the two. We may conclude, therefore, that *in these experiments the resistance which the medium offers to the motion of a body through it is not sensibly increased when the body becomes electrically charged. This demonstrates experimentally the exact validity for this work of the assumption made on p. 70 that the velocity of the drop is strictly proportional to the force acting upon it, whether it is charged or uncharged.*

The result is at first somewhat surprising since, according to Sutherland's theory of the small ion, the small mobility or diffusivity of charged molecules, as compared with uncharged, is due to the additional resistance which the medium offers to the motion through it of a charged molecule. This additional resistance is due to the fact that the charge on a molecule drags into collision with it more molecules than would otherwise hit it. But with oil drops of the sizes here used

( $a = 50 \times 10^{-6}$ ) the total number of molecular collisions against the surface of the drop is so huge that even though the small number of charges on it might produce a few more collisions, their number would be negligible in comparison with the total number. At any rate the experiment demonstrates conclusively that the charges on our oil drops do not influence the resistance of the medium to the motion of the drop. This conclusion might also have been drawn from the data contained in Table VI. The evidence for its absolute correctness has been made more convincing still by a comparison of drops which carried but 1 charge and those which carried as many as 68 unit charges. Further, I have observed the rate of fall under gravity of droplets which were completely discharged, and in every case that I have ever tried I have found this rate precisely the same, within the limits of error of the time measurements, as when it carried 8 or 10 unit charges.

## VII. DROPS ACT LIKE RIGID SPHERES

It was of very great importance for the work, an account of which will be given in the next chapter to determine whether the drops ever suffer—either because of their motion through a resisting medium, or because of the electrical field in which they are placed—any appreciable distortion from the spherical form which a freely suspended liquid drop must assume. The complete experimental answer to this query is contained in the agreement of the means at the bottom of the last and the third from the last columns in Table VI and in similar agreements shown in many other tables, which



may be found in the original articles.<sup>1</sup> Since  $\frac{1}{t_g}$  is in this experiment large compared to  $\frac{1}{t_F}$ , the value of the greatest common divisor at the bottom of the last column of Table VI is determined almost wholly by the rate of fall of the particle under gravity when there is no field at all between the plates, while the velocity at the bottom of the third from the last column is a difference between two velocities in a strong electrical field. If, therefore, the drop were distorted by the electrical field, so that it exposed a larger surface to the resistance of the medium than when it had the spherical form, the velocity due to a given force, that is, the velocity given at the bottom of the third from the last column, would be less than that found at the bottom of the last column, which corresponds to motions when the drop certainly was spherical.

Furthermore, if the drops were distorted by their motion through the medium, then this distortion would be greater for high speeds than for low, and consequently the numbers in the third from the last column would be consistently larger for high speeds than for low. No such variation of these numbers with speed is apparent either in Table VI or in other similar tables.

We have then in the exactness and invariableness of the multiple relations shown by successive differences in speed and the successive sums of the speeds in the third from the last and the last columns of Table VI complete experimental proof that in this work the droplets act under all circumstances like undeformed spheres. It is of interest that Professor Hadamard,<sup>2</sup> of the University of

<sup>1</sup> *Phys. Rev.*, Series 1, XXXII (1911), 349; Series 2, II (1913), 109.

<sup>2</sup> *Comptes rendus* (1911), 1735.



Paris, and Professor Lunn,<sup>1</sup> of the University of Chicago, have both shown from theoretical considerations that this would be the case with oil drops as minute as those with which these experiments deal, so that the conclusion may now be considered as very firmly established both by the experimentalist and the theorist.

<sup>1</sup> *Phys. Rev.*, XXXV (1912), 227.

## CHAPTER V

### THE EXACT EVALUATION OF $e$

#### I. DISCOVERY OF THE FAILURE OF STOKES'S LAW

Although complete evidence for the atomic nature of electricity is found in the fact that all of the charges which can be placed upon a body as measured by the sum of speeds  $v_1 + v_2$ , and all the changes of charge which this body can undergo as measured by the differences of speed ( $v'_2 - v_2$ ) are invariably found to be exact multiples of a particular speed, yet there is something still to be desired if we must express this greatest common divisor of all the observed series of speeds merely as a velocity which is a characteristic constant of each particular drop but which varies from drop to drop. We ought rather to be able to reduce this greatest common divisor to electrical terms by finding the proportionality factor between speed and charge, and, that done, we should, of course, expect to find that the charge came out a universal constant independent of the size or kind of drop experimented upon. The attempt to do this by the method which I had used in the case of the water drops (p. 55), namely, by the assumption of Stokes's Law, heretofore taken for granted by all observers, led to the interesting discovery that this law is not valid.<sup>1</sup> Accord-

<sup>1</sup>Cunningham (*Proc. Roy. Soc.*, LXXXIII [1910], 357) and the author came independently to the conclusion as to the invalidity of Stokes's Law, he from theoretical considerations developed at about the same time, I from my experimental work.

ing to this law the rate of fall of a spherical drop under gravity, namely,  $v_1$ , is given by

$$v_1 = \frac{2ga^2}{9\eta}(\sigma - \rho) \dots\dots\dots (11)$$

in which  $\eta$  is the viscosity of the medium,  $a$  the radius and  $\sigma$  the density of the drop, and  $\rho$  the density of the medium. This last quantity was neglected in (6), p. 55, because, with the rough measurements there possible, it was useless to take it into account, but with our oil drops in dry air all the other factors could be found with great precision.

When we assume the foregoing equation of Stokes and combine it with equation (5) on p. 55, an equation whose exact validity was proved experimentally in the last chapter, we obtain, after substitution of the purely geometrical relation  $m = \frac{4\pi}{3}a^3(\sigma - \rho)$ , the following expression for the charge  $e_n$  carried by a drop loaded with  $n$  electrons which we will assume to have been counted by the method described:

$$e_n = \frac{4\pi}{3} \left( \frac{9\eta}{2} \right)^{\frac{3}{2}} \left( \frac{1}{g(\sigma - \rho)} \right)^{\frac{1}{2}} \frac{(v_1 + v_2)v_1^{\frac{1}{2}}}{F} \dots\dots\dots (12)$$

According to this equation the elementary charge  $e_1$  should be obtained by substituting in this the greatest common divisor of all the observed series of values of  $(v_1 + v_2)$  or of  $(v'_2 - v_2)$ . Thus, if we call this  $(v_1 + v_2)_0$ , we have

$$e_1 = \frac{4\pi}{3} \left( \frac{9\eta}{2} \right)^{\frac{3}{2}} \left( \frac{1}{g(\sigma - \rho)} \right)^{\frac{1}{2}} \frac{(v_1 + v_2)_0 v_1^{\frac{1}{2}}}{F} \dots\dots\dots (13)$$

But when this equation was tested out upon different drops, although it yielded perfectly concordant results

so long as the different drops all fell with about the same speed, when drops of different speeds, and, therefore, of different sizes, were used, the values of  $e_1$  obtained were consistently larger the smaller the velocity under gravity. For example,  $e_1$  for one drop for which  $v_1 = .01085$  cm. per second came out  $5.49 \times 10^{-10}$ , while for another of almost the same speed, namely,  $v_1 = .01176$ , it came out  $5.482$ ; but for two drops whose speeds were five times as large, namely,  $.0536$  and  $.0553$ ,  $e_1$  came out  $5.143$  and  $5.145$ , respectively. This could mean nothing save that Stokes's Law did not hold for drops of the order of magnitude here used, something like  $a = .0002$  cm. (see Section IV below), and it was surmised that the reason for its failure lay in the fact that the drops were so small that they could no longer be thought of as moving through the air as they would through a continuous homogeneous medium, which was the situation contemplated in the deduction of Stokes's Law. This law ought to begin to fail as soon as the inhomogeneities in the medium—i.e., the distances between the molecules—began to be at all comparable with the dimensions of the drop. Furthermore, it is easy to see that as soon as the holes in the medium begin to be comparable with the size of the drop, the latter must begin to increase its speed, for it may then be thought of as beginning to reach the stage in which it can fall freely through the holes in the medium. This would mean that the observed speed of fall would be more and more in excess of that given by Stokes's Law the smaller the drop became. But the apparent value of the electronic charge, namely,  $e_1$ , is seen from equation (13) to vary directly with the speed  $(v_1 + v_2)_0$  imparted by a given force. Hence  $e_1$  should

come out larger and larger the smaller the radius of the drop, that is, the smaller its velocity under gravity. Now, this was exactly the behavior shown consistently by all the oil drops studied. Hence it looked as though we had discovered, not merely the failure of Stokes's Law, but also the line of approach by means of which it might be corrected.

In order to be certain of our ground, however, we were obliged to initiate a whole series of new and somewhat elaborate experiments.

These consisted, first, in finding very exactly what is the coefficient of viscosity of air under conditions in which it may be treated as a homogeneous medium, and, second, in finding the limits within which Stokes's Law may be considered valid.

## II. THE COEFFICIENT OF VISCOSITY OF AIR

The experiments on the coefficient of viscosity of air were carried out in the Ryerson Laboratory by Dr. Lachen Gilchrist,<sup>1</sup> and Dr. I. M. Rapp.<sup>2</sup> Dr. Gilchrist used a method which was in many respects new and which may fairly be said to be freer from theoretical uncertainties than any method which has ever been used. He estimated that his results should not be in error by more than .1 or .2 of 1 per cent. Dr. Rapp used a form of the familiar capillary-tube method, but under conditions which seemed to adapt it better to an absolute evaluation of  $\eta$  for air than capillary-tube arrangements have ordinarily been.

<sup>1</sup> *Phys. Rev.*, N.S., I, (1913), 124.

<sup>2</sup> *Phys. Rev.*, N.S., II (1913), 363.

These two men, as the result of measurements which were in progress for more than two years, obtained final means which were in very close agreement with one another as well as with the most careful of preceding determinations. It will be seen from Table IX that

TABLE IX

$\eta_{23}$ for Air	
.00018227	Rapp, Capillary-tube method, 1913 ( <i>Phys. Rev.</i> , II, 363).
.00018257	Gilchrist, Constant deflection method, 1913 ( <i>Phys. Rev.</i> , I, 124).
.00018229	Hogg, Damping of oscillating cylinders, 1905 ( <i>Proc. Am. Acad.</i> , XL, 611).
.00018258	Tomlinson, Damping of Swinging Pendulum, 1886 ( <i>Phil. Trans.</i> , CLXXVII, 767).
.00018232	Grindley and Gibson, Flow through pipe, 1908 ( <i>Proc. Roy. Soc.</i> , LXXX, 114).
Mean. . .	.00018240

every one of the five different methods which have been used for the absolute determination of  $\eta$  for air leads to a value that differs by less than one part in one thousand from the following mean value,  $\eta_{23} = .00018240$ . It was concluded, therefore, that we could depend upon the value of  $\eta$  for the viscosity of air under the conditions of our experiment to at least one part in one thousand. Very recently Dr. E. Harrington<sup>1</sup> has improved still further the apparatus designed by Dr. Gilchrist and the author and has made with it in the Ryerson Laboratory a determination of  $\eta$  which is, I think, altogether unique in its reliability and precision. I give to it alone greater

<sup>1</sup> *Phys. Rev.*, December, 1916.

weight than to all the other work of the past fifty years in this field taken together. The final value is

$$\eta_{23} = .00018226$$

and the error can scarcely be more than one part in two thousand.

### III. LIMITS OF VALIDITY OF STOKES'S LAW

In the theoretical derivation of Stokes's Law the following five assumptions are made: (1) that the inhomogeneities in the medium are small in comparison with the size of the sphere; (2) that the sphere falls as it would in a medium of unlimited extent; (3) that the sphere is smooth and rigid; (4) that there is no slipping of the medium over the surface of the sphere; (5) that the velocity with which the sphere is moving is so small that the resistance to the motion is all due to the viscosity of the medium and not at all due to the inertia of such portion of the media as is being pushed forward by the motion of the sphere through it.

If these conditions were all realized then Stokes's Law ought to hold. Nevertheless, there existed up to the year 1910 no experimental work which showed that actual experimental results may be accurately predicted by means of the unmodified law, and Dr. H. D. Arnold accordingly undertook in the Ryerson Laboratory to test how accurately the rates of fall of minute spheres through water and alcohol might be predicted by means of it.

His success in these experiments was largely due to the ingenuity which he displayed in producing accurately spherical droplets of rose-metal. This metal melts at about 82° C. and is quite fluid at the temperature of



boiling water. Dr. Arnold placed some of this metal in a glass tube drawn to form a capillary at one end and suspended the whole of the capillary tube in a glass tube some 70 cm. long and 3 cm. in diameter. He then filled the large tube with water and applied heat in such a way that the upper end was kept at about  $100^{\circ}$  C., while the lower end was at about  $60^{\circ}$ . He then forced the molten metal, by means of compressed air, out through the capillary into the hot water. It settled in the form of spray, the drops being sufficiently cooled by the time they reached the bottom to retain their spherical shape. This method depends for its success on the relatively slow motion of the spheres and on the small temperature gradient of the water through which they fall. The slow and uniform cooling tends to produce homogeneity of structure, while the low velocities allow the retention of very accurately spherical shape. In this way Dr. Arnold obtained spheres of radii from .002 cm. to .1 cm., which, when examined under the microscope, were found perfectly spherical and practically free from surface irregularities. He found that the slowest of these drops fell in liquids with a speed which could be computed from Stokes's Law with an accuracy of a few tenths of 1 per cent, and he determined experimentally the limits of speed through which Stokes's Law was valid.

Of the five assumptions underlying Stokes's Law, the first, third, and fourth were altogether satisfied in Dr. Arnold's experiment. The second assumption he found sufficiently realized in the case of the very smallest drops which he used, but not in the larger ones. The question, however, of the effect of the walls of the vessel upon the motion of drops through the liquid contained

in the vessel had been previously studied with great ability by Ladenburg,<sup>1</sup> who, in working with an exceedingly viscous oil, namely Venice turpentine, obtained a formula by which the effects of the wall on the motion might be eliminated. If the medium is contained in a cylinder of circular cross-section of radius  $R$  and of length  $L$ , then, according to Ladenburg, the simple Stokes formula should be modified to read

$$V = \frac{2}{9} \frac{ga^2(\sigma - \rho)}{\eta \left(1 + 2.4 \frac{a}{R}\right) \left(1 + 3.1 \frac{a}{L}\right)}.$$

Arnold found that this formula held accurately in all of his experiments in which the walls had any influence on the motion. Thus he worked under conditions under which all of the first four assumptions underlying Stokes's Law were taken care of. This made it possible for him to show that the law held rigorously when the fifth assumption was realized, and also to find by experiment the limits within which this last assumption might be considered as valid. Stokes had already found from theoretical considerations<sup>2</sup> that the law would not hold unless the radius of the sphere were small in comparison with  $\frac{\eta}{v\rho}$ , in which  $\rho$  is the density of the medium,  $\eta$  its viscosity, and  $v$  the velocity of the sphere. This radius is called the critical radius. But it was not known how near it was possible to approach to the critical radius. Arnold's experiments showed that the inertia of the medium has no appreciable effect upon the rate of

<sup>1</sup> *Ann. der Phys.*, XXII (1907), 287; XXIII (1908), 447.

<sup>2</sup> *Math. and Phys. Papers*, III, 59.

motion of a sphere so long as the radius of that sphere is less than .6 of the critical radius.

Application of this result to the motion of our oil drops established the fact that even the very fastest drops which we ever observed fell so slowly that not even a minute error could arise because of the inertia of the medium. This meant that the fifth condition necessary to the application of Stokes's Law was fulfilled. Furthermore, our drops were so small that the second condition was also fulfilled, as was shown by the work of both Ladenburg and Arnold. The third condition was proved in the last chapter to be satisfied in our experiments. Since, therefore, Arnold's work had shown very accurately that Stokes's Law does hold when all of the five conditions are fulfilled, the problem of finding a formula for replacing Stokes's Law in the case of our oil-drop experiments resolved itself into finding in just what way the failure of assumptions 1 and 4 affected the motion of these drops.

#### IV. CORRECTION OF STOKES'S LAW FOR INHOMOGENEITIES IN THE MEDIUM

The first procedure was to find how badly Stokes's Law failed in the case of our drops. This was done by plotting the apparent value of the electron  $e_r$  against the observed speed under gravity. This gave the curve shown in Fig. 4, which shows that though for very small speeds  $e_r$  varies rapidly with the change in speed, for speeds larger than that corresponding to the abscissa marked 1,000 there is but a slight dependence of  $e_r$  on speed. This abscissa corresponds to a speed of .1 cm. per second. We may then conclude that for drops which

are large enough to fall at a rate of 1 cm. in ten seconds or faster, Stokes's Law needs but a small correction, because of the inhomogeneity of the air.

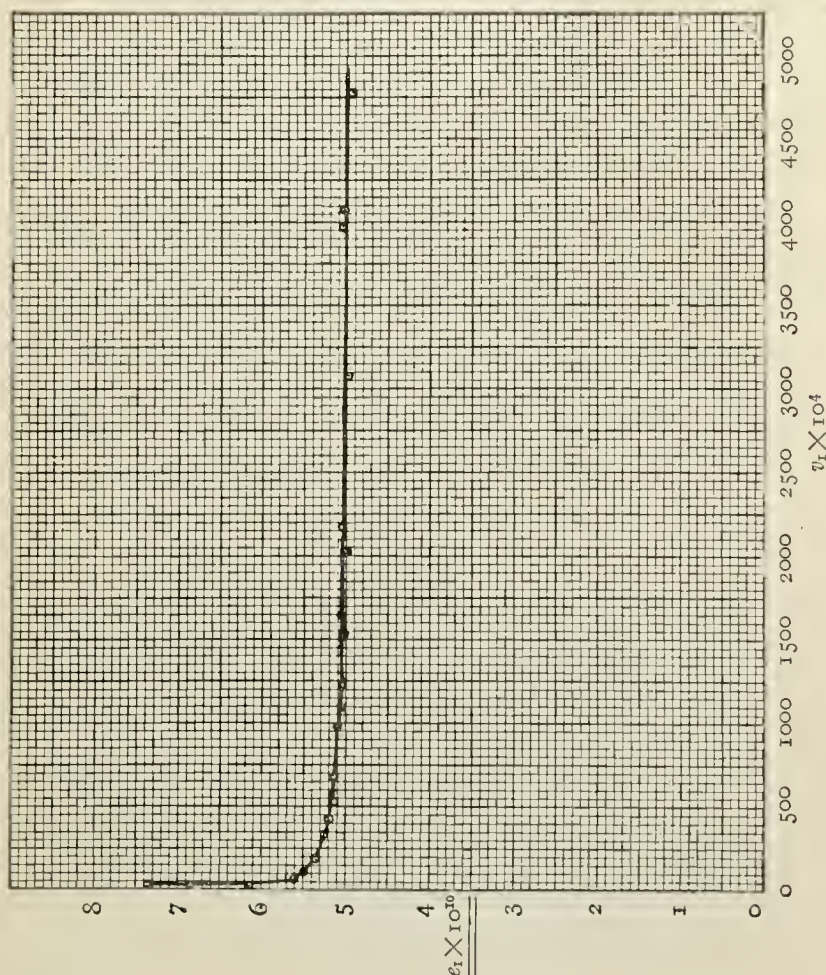


FIG. 4

To find an exact expression for this correction we may proceed as follows: The average distance which a gas molecule goes between two collisions with its neighbors, a quantity well known and measured with some approach

to precision in physics and called "the mean free path" of a gas molecule, is obviously a measure of the size of the holes in a gaseous medium. When Stokes's Law begins to fail as the size of the drops diminish, it must be because the medium ceases to be homogeneous, as looked at from the standpoint of the drop, and this means simply that the radius of the drop has begun to be comparable with the mean size of the holes—a quantity which we have decided to take as measured by the mean free path  $l$ . The increase in the speed of fall over that given by Stokes's Law, when this point is reached, must then be some function of  $\frac{l}{a}$ . In other words, the correct expression for the speed  $v_1$  of a drop falling through a gas, instead of being

$$v_1 = \frac{2}{9} \frac{ga^2}{\eta} (\sigma - \rho),$$

as Arnold showed that it was when the holes were negligibly small—as the latter are when the drop falls through a liquid—should be of the form

$$v_1 = \frac{2}{9} \frac{ga^2}{\eta} (\sigma - \rho) \left( 1 + f \frac{l}{a} \right) \dots \dots \dots (14)$$

If we were in complete ignorance of the form of the function  $f$  we could still express it in terms of a series of undetermined constants  $A$ ,  $B$ ,  $C$ , etc., thus

$$f = A \frac{l}{a} + B \left( \frac{l}{a} \right)^2 + C \left( \frac{l}{a} \right)^3, \text{ etc.,}$$

and so long as the departures from Stokes's Law were small as Fig. 4 showed them to be for most of our drops,



we could neglect the second-order terms in  $\frac{l}{a}$  and have therefore

$$v_1 = \frac{2}{9} \frac{g a^2}{\eta} (\sigma - \rho) \left( 1 + A \frac{l}{a} \right) \dots \dots \dots (15)$$

Using this corrected form of Stokes's Law to combine with (9) (p. 20), we should obviously get the charge  $e_n$  in just the form in which it is given in (13), save that wherever a velocity appears in (13) we should now have

to insert in place of this velocity  $\frac{v}{1 + A \frac{l}{a}}$ . And since the

velocity of the drop appears in the  $3/2$  power in (13), if we denote now by  $e$  the absolute value of the electron and by  $e_1$ , as heretofore, the apparent value obtained from the assumption of Stokes's Law, that is, from the use of (13), we obtain at once

$$e = \frac{e_1}{\left( 1 + A \frac{l}{a} \right)^{\frac{3}{2}}} \dots \dots \dots (16)$$

In this equation  $e_1$  can always be obtained from (13), while  $l$  is a known constant, but  $e$ ,  $A$ , and  $a$  are all unknown. If  $a$  can be found our observations permit at once of the determination of both  $e$  and  $A$ , as will be shown in detail under Section VI (see p. 105).

However, the possibility of determining  $e$  if we know  $a$  can be seen in a general way without detailed analysis. For the determination of the radius of the drop is equivalent to finding its weight, since its density is known. That we can find the charge on the drop as soon as we can determine its weight is clear from the simple consideration that the velocity under gravity is proportional to its weight, while the velocity in a given

electrical field is proportional to the charge which it carries. Since we measure these two velocities directly, we can obtain either the weight, if we know the charge, or the charge, if we know the weight. (See equation 9, p. 70.)

## V. WEIGHING THE DROPLET

The way which was first used for finding the weight of the drop was simply to solve Stokes's uncorrected equation (11) (p. 91) for  $a$  in the case of each drop. Since the curve of Fig. 4 shows that the departures from Stokes's Law are small except for the extremely slow drops, and since  $a$  appears in the second power in (11), it is clear that, if we leave out of consideration the very slowest drops, (11) must give us very nearly the correct values of  $a$ . We can then find the approximate value of  $A$  by the method of the next section, and after it is found we can solve (15) for the correct value of  $a$ . This is a method of successive approximations which theoretically yields  $a$  and  $A$  with any desired degree of precision. As a matter of fact the whole correction term,  $A \frac{l}{a}$  is a small one, so that it is never necessary to make more than two approximations to obtain  $a$  with much more precision than is needed for the exact evaluation of  $e$ .

As soon as  $e$  was fairly accurately known it became possible, as indicated above, to make a direct weighing of extraordinarily minute bodies with great certainty and with a very high degree of precision. For we have already shown experimentally that the equation

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \dots\dots\dots (17)$$



is a correct one and it involves no assumption whatever as to the shape, or size, or material of the particle. If we solve this equation for the weight  $mg$  of the particle we get

$$mg = F e_n \frac{v_1}{v_1 + v_2} \dots \dots \dots (18)$$

In this equation  $e_n$  is known with the same precision as  $e$ , for we have learned how to count  $n$ . It will presently be shown that  $e$  is probably now known with an accuracy of one part in a thousand, hence  $mg$  can now be determined with the same accuracy for any body which can be charged up with a counted number  $n$  of electrons and then pulled up against gravity by a known electrical field, or, if preferred, simply balanced against gravity after the manner used in the water-drop experiment and also in part of the oil-drop work.<sup>1</sup> *This device is simply an electrical balance in place of a mechanical one, and it will weigh accurately and easily to one ten-billionth of a milligram.*

Fifty years ago it was considered the triumph of the instrument-maker's art that a balance had been made so sensitive that one could weigh a piece of paper, then write his name with a hard pencil on the paper and determine the difference between the new weight and the old—that is, the weight of the name. This meant determining a weight as small as one-tenth or possibly one-hundredth of a milligram (a milligram is about 1/30,000 of an ounce). Some five years ago Ramsay and Spencer, in London, by constructing a balance entirely out of very fine quartz fibers and placing it in a vacuum, succeeded in weighing objects as small

<sup>1</sup> See *Phil. Mag.*, XIX (1910), 216; XXI (1911), 757.

as one-millionth of a milligram, that is, they pushed the limit of the weighable down about ten thousand times. The work which we are now considering pushed it down at least ten thousand times farther and made it possible to weigh accurately bodies so small as not to be visible at all to the naked eye. For it is only necessary to float such a body in the air, render it visible by reflected light in an ultra-microscope arrangement of the sort we were using, charge it electrically by the capture of ions, count the number of electrons in its charge by the method described, and then vary the potential applied to the plates or the charge on the body until its weight is just balanced by the upward pull of the field. The weight of the body is then exactly equal to the product of the known charge by the strength of the electric field. We made all of our weighings of our drops and the determination of their radii in this way as soon as we had located  $e$  with a sufficient degree of precision to warrant it.<sup>1</sup> Indeed, even before  $e$  is very accurately known it is possible to use such a balance for a fairly accurate evaluation of the radius of a spherical drop. For when we replace  $m$  in (18) by  $4/3\pi\bar{n}a^3(\sigma-\rho)$  and solve for  $a$  we obtain

$$a = \sqrt[3]{\frac{3Fe_n}{4\pi g(\sigma-\rho)} \frac{v_1}{v_1+v_2}} \dots\dots\dots (19)$$

The substitution in this equation of an approximately correct value of  $e$  yields  $a$  with an error but one-third as great as that contained in the assumed value of  $e$ , for  $a$  is seen from this equation to vary as the cube root of  $e$ . This is the method which, in view of the accurate evalua-

<sup>1</sup> *Phys. Rev.*, II (1913), 117. This paper was read before the Deutsche physikalische Gesellschaft in Berlin in June, 1912.

tion of  $e$ , it is now desirable to use for the determination of the weight or dimensions of any minute body, for the method is quite independent of the nature of the body or of the medium in which it is immersed. Indeed, it constitutes as direct and certain a weighing of the body as though it were weighed on a mechanical balance.

## VI. THE EVALUATION OF $e$ AND $A$

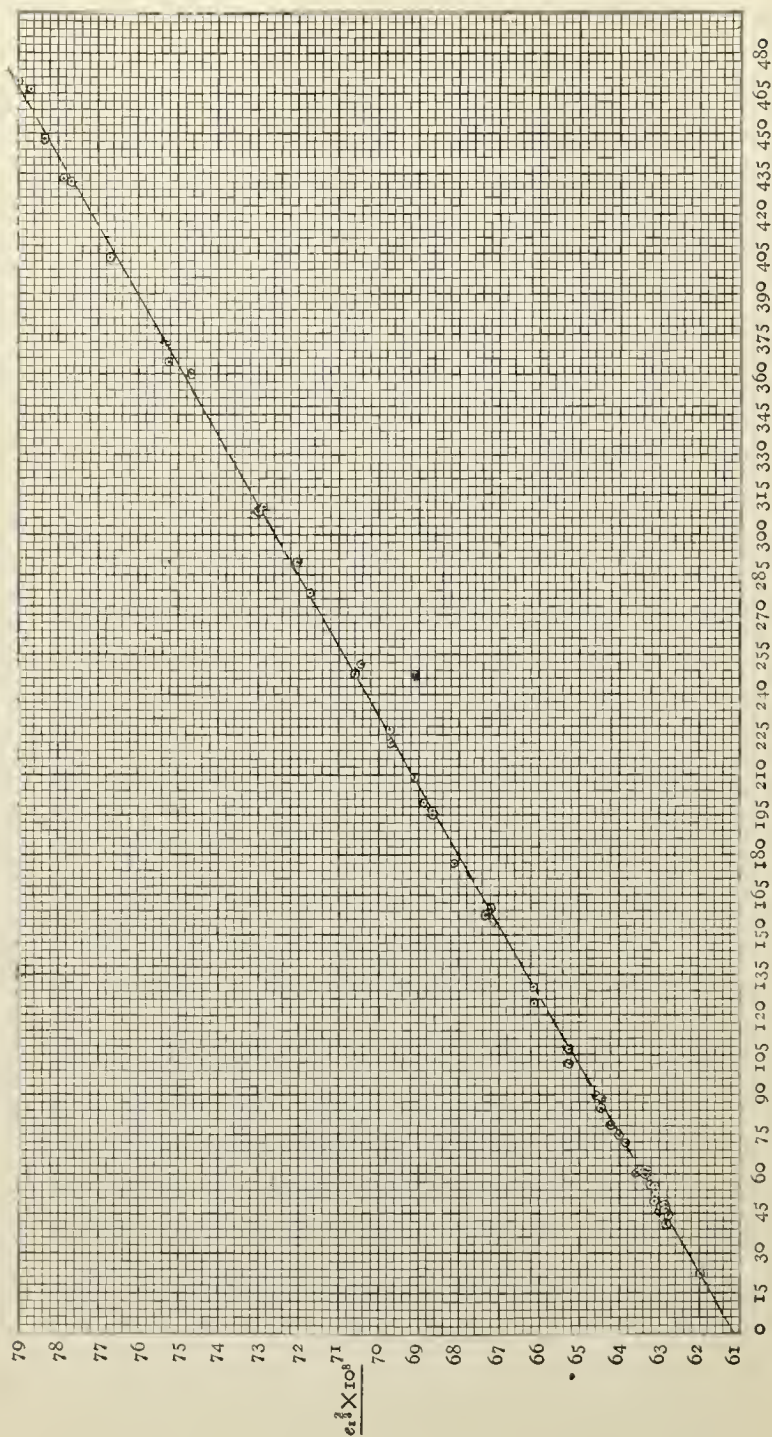
With  $e_1$  and  $\frac{l}{a}$  known, we can easily determine  $e$  and  $A$  from the equation

$$e = \frac{e_1}{\left(1 + A \frac{l}{a}\right)^{\frac{3}{2}}}$$

for if we write this equation in the form

$$e_1^2 \left(1 + A \frac{l}{a}\right) = e_1^{\frac{2}{3}} \dots \dots \dots (20)$$

and then plot the observed values of  $e_1$  as ordinates and the corresponding values of  $\frac{l}{a}$  as abscissae we should get a straight line, provided our corrected form of Stokes's Law (15) (p. 101) is adequate for the correct representation of the phenomena of fall of the droplets within the range of values of  $\frac{l}{a}$  in which the experiments lie. If no such linear relation is found, then an equation of the form of (15) is not adequate for the description of the phenomena within this range. As a matter of fact, a linear relation was found to exist for a much wider range of values of  $\frac{l}{a}$  than was anticipated would be the case. The



$$\frac{1}{\rho u}$$

FIG. 5



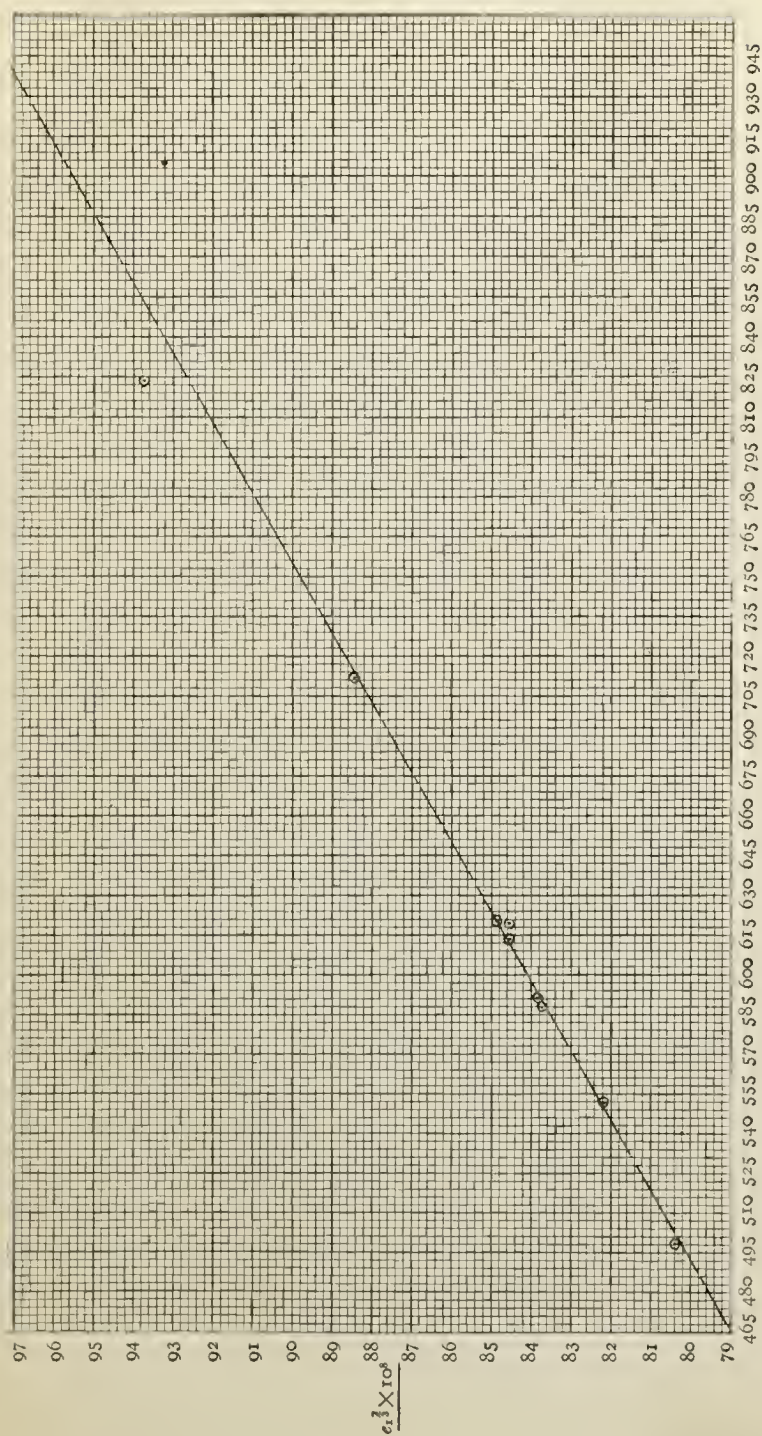


FIG. 6

intercept of this line on the axis of ordinates, that is, the value of  $e_1$  when  $\frac{l}{a}=0$  is seen from (20) to be  $e^{\frac{2}{3}}$ , and we have but to raise this to the  $3/2$  power to obtain the absolute value of  $e$ . Again,  $A$  is seen from (20) to be merely the slope of this line divided by the intercept on the  $e_1^{\frac{2}{3}}$  axis.

In order to carry this work out experimentally it is necessary to vary  $\frac{l}{a}$  and find the corresponding values of  $e_1$ . This can be done in two ways. First, we may hold the pressure constant and choose smaller and smaller drops with which to work, or we may work with drops of much the same size but vary the pressure of the gas in which our drops are suspended, for the mean free path  $l$  is evidently inversely proportional to the pressure.

Both procedures were adopted, and it was found that a given value of  $e_1$  always corresponded to a given value of  $\frac{l}{a}$ , no matter whether  $l$  was kept constant and  $a$  reduced to, say, one-tenth of its first value, or  $a$  kept about the same and  $l$  multiplied tenfold. The result of one somewhat elaborate series of observations which was first presented before the Deutsche physikalische Gesellschaft in June, 1912, and again before the British Association at Dundee in September, 1912,<sup>1</sup> is shown in Figs. 5 and 6. The numerical data from which these curves are plotted are given fairly fully in Table IX. It will be seen that this series of observations embraces a study of 58 drops. These drops represent all of those studied for 60 consecutive days, no single one being

<sup>1</sup> *Phys. Rev.*, II (1913), 136.



TABLE IX

No.	Tem. °C.	P.D. (Volts)	$t_g$ (Sec.)	$v_t$ cm./sec.	$(v_1 + v_2)_0$	$n$	$a \times 10^{15}$ cm.	$p$ (cm. Hg)	$\frac{I}{pa}$	$\frac{l}{a}$	$e_1 \times 10^{10}$	$e_2 \times 10^8$	$e_3 \times 10^8$
1....	23.00	5.168	4.303	.2357	.003203	77-102	58.56	75.80	22.52	.01615	4.877	61.90	61.14
2....	22.80	5.120	8.492	.1202	.004670	27-36	32.64	75.00	40.85	.02933	4.981	62.82	61.20
3....	23.46	5.100	9.905	.1032	.004996	22-27	30.29	73.71	44.88	.03212	4.971	62.75	61.04
4....	22.85	5.103	10.758	.09489	.005211	18-36	28.94	75.20	45.92	.03288	5.001	63.00	61.24
5....	23.08	5.072	10.663	.09575	.005476	20-30	20.14	73.25	46.85	.03353	4.982	62.82	61.13
6....	22.82	5.085	11.880	.08584	.005497	17-24	27.54	75.62	48.11	.03437	4.901	62.93	61.09
7....	23.79	5.090	11.950	.08368	.005480	19-22	27.57	75.10	48.44	.03466	4.981	62.82	61.07
8....	23.50	5.158	12.540	.08141	.005023	10-19	26.90	75.30	49.52	.03544	5.016	63.12	61.23
9....	22.87	5.139	13.562	.07375	.005062	19-23	25.71	75.00	51.73	.03702	5.016	63.13	61.15
10....	23.25	5.015	15.380	.06641	.006174	13-22	24.31	76.27	54.09	.03871	5.010	63.08	61.02
11....	23.01	5.066	15.103	.06720	.006087	11-14	24.36	73.90	55.52	.03973	5.015	63.12	61.00
12....	23.00	5.086	15.985	.06575	.006416	12-16	23.70	75.14	56.15	.04018	5.028	63.24	61.10
13....	23.00	5.024	15.695	.05403	.006873	9-15	21.91	76.06	59.94	.04290	5.043	63.35	61.00
14....	23.09	5.077	18.730	.05451	.006988	8-16	21.85	75.28	60.78	.04348	5.064	63.53	61.21
15....	23.85	5.078	18.959	.05274	.006966	8-18	21.87	75.24	61.03	.04368	5.040	63.33	61.07
16....	23.70	5.103	18.738	.05449	.007005	9-16	21.87	74.68	61.33	.04390	5.065	63.54	61.21
17....	23.06	5.000	18.415	.05545	.006890	9-18	22.06	73.47	61.09	.04411	5.054	63.43	61.00
18....	22.83	5.003	26.130	.03907	.008339	5-13	18.45	75.54	71.74	.03134	5.098	63.82	61.68
19....	22.95	5.033	28.568	.03570	.008051	5-9	17.63	75.87	74.77	.03350	5.120	64.00	61.12
20....	23.00	5.004	9.480	.10772	.005958	23-32	39.54	41.77	78.40	.05612	5.145	64.22	61.23
21....	23.08	5.018	35.253	.02893	.006600	4-11	15.86	74.32	85.08	.06089	5.166	64.36	61.11
22....	23.22	5.005	40.542	.02515	.010332	3-9	14.75	76.42	88.70	.06350	5.168	64.40	61.01
23....	22.76	5.098	39.900	.02554	.010510	3-6	14.85	75.40	89.35	.06395	5.190	64.59	61.18
24....	23.16	5.059	12.466	.08189	.005806	15-28	26.44	37.19	101.8	.07283	5.269	65.24	61.35
25....	22.98	5.066	15.157	.06737	.006399	12-17	24.01	38.95	107.2	.07600	5.278	65.28	61.20
26....	23.20	4.572	7.875	.12986	.004324	33-40	33.07	24.33	124.4	.08892	5.379	66.06	61.31
27....	23.18	4.570	9.408	.1085	.004730	23-29	30.23	25.37	130.4	.09030	5.381	66.16	61.18
28....	23.00	5.145	84.270	.1211	.01595	1-4	4.69	75.83	130.3	.09322	5.379	66.14	61.16
29....	22.99	5.073	23.223	.04393	.008488	6-12	19.06	33.47	156.8	.1117	5.529	67.36	61.37

Mean = 61.120

Mean  
61.138

TABLE IX—Continued

No.	Tem. °C.	P.D. (Volts)	$t_g$ (Sec.)	$v$ cm./sec.	$(v_1 + v_2)_0$	$n$	$a \times 10^{10}$ cm.	$p$ (cm. Hg).	$\frac{1}{pa}$	$\frac{l}{a}$	$e_1 \times 10^{10}$	$e_2^3 \times 10^8$	$e_3^3 \times 10^8$	$e^2 \times 10^8$
30....	23.19	5.000	26.830	.03801	.000111	5-10	17.77	35.18	160.2	.1147	5.507	67.18	67.18	61.06
31....	22.80	5.008	38.479	.02649	.011180	3-5	14.71	35.51	176.5	.1263	5.621	68.12	68.12	61.38
32....	23.06	5.070	14.000	.07246	.000702	12-17	24.29	21.12	195.0	.1394	5.602	68.67	68.67	61.22
33....	23.07	4.582	18.229	.05601	.000981	10-13	21.33	23.86	106.6	.1405	5.687	68.64	68.64	61.13
34....	23.06	5.061	38.010	.02682	.011205	3-8	14.72	34.01	109.8	.1429	5.714	68.84	68.84	61.20
35....	23.00	4.246	9.265	.11032	.004653	27-34	20.84	10.00	209.5	.1499	5.739	69.07	69.07	61.07
36....	22.01	4.236	9.879	.10340	.004803	24-28	28.74	15.67	222.0	.1589	5.820	69.71	69.71	61.23
37....	23.06	4.236	12.040	.08496	.005362	18-24	26.27	16.75	227.5	.1625	5.821	69.72	69.72	61.03
38....	22.94	2.556	10.657	.09581	.003109	32-43	27.49	14.70	247.5	.1771	5.935	70.61	70.61	61.16
39....	23.00	5.054	19.950	.05115	.008370	8-15	20.12	10.73	251.8	.1802	5.910	70.41	70.41	60.79
40....	23.05	5.058	21.130	.04830	.008865	7-9	18.38	18.54	276.3	.1993	6.076	71.72	71.72	61.09
41....	23.05	5.062	24.008	.04254	.009496	6-8	18.16	19.01	280.6	.2073	6.110	72.03	72.03	60.97
42....	22.94	4.238	18.347	.05504	.007110	9-17	20.60	15.72	308.8	.2210	6.224	73.04	73.04	61.24
43....	23.18	3.254	13.909	.07340	.004720	16-28	23.70	13.55	311.0	.2227	6.214	72.83	72.83	60.95
44....	23.04	4.231	29.114	.03593	.009273	5-9	16.16	17.17	360.6	.2579	6.466	74.77	74.77	61.00
45....	22.87	3.317	20.776	.03435	.007439	5-12	15.90	17.27	304.2	.2606	6.537	75.30	75.30	61.39
46....	22.81	3.401	25.909	.03937	.007311	6-19	16.90	14.68	403.3	.2886	6.710	76.71	76.71	61.30
47....	22.83	2.550	12.891	.07921	.003935	18-42	23.80	9.70	432.8	.3007	6.841	77.66	77.66	61.13
48....	22.80	2.559	32.326	.03159	.006286	7-14	15.01	15.35	433.8	.3104	6.866	77.85	77.85	61.28
49....	23.02	3.370	14.083	.06815	.011333	8-9	22.00	8.00	466.7	.3221	6.936	78.36	78.36	61.22
50....	23.45	2.535	11.659	.08757	.003793	25-30	24.88	8.06	466.7	.3310	6.978	78.67	78.67	60.85
51....	23.48	2.539	10.924	.09334	.003015	25-30	24.88	8.06	466.7	.3310	6.978	78.67	78.67	60.85
52....	22.98	3.351	50.400	.02021	.010775	2-6	25.69	8.26	470.7	.3368	7.024	79.02	79.02	61.04
53....	23.16	2.451	33.379	.03955	.006023	2-6	11.83	16.95	468.5	.3568	7.210	80.40	80.40	61.36
54....	23.46	2.537	10.227	.05347	.005347	5-10	14.39	12.61	511.3	.3945	7.470	82.19	82.19	61.13
55....	22.00	2.540	24.254	.04206	.006031	11-17	18.87	9.93	537.8	.4112	7.601	83.73	83.73	61.18
56....	23.21	1.700	5.058	.20350	.000314	9-18	16.72	10.11	591.5	.4233	7.672	84.57	84.57	61.11
57....	23.12	2.321	15.473	.06599	.004801	117-136	36.53	4.46	614.2	.4366	7.777	84.57	84.57	60.87
58....	23.03	3.388.5	24.33	.04196	.008183	18-24	20.85	7.74	619.7	.4435	7.774	84.54	84.54	60.87
						6-10	16.62	9.070	620.2	.4439	7.810	84.83	84.83	61.14

Mean of all numbers in last column = 61.138

Mean of first 23 numbers = 61.120

Mean = 61.138

omitted. They represent a thirty-fold variation in  $\frac{l}{a}$  (from .016, drop No. 1, to .444, drop No. 58), a seven-teen-fold variation in the pressure  $p$  (from 4.46 cm., drop No. 56, to 76.27 cm., drop No. 10), a twelvefold variation in  $a$  (from  $4.69 \times 10^{-5}$  cm., drop No. 28, to  $58.56 \times 10^{-5}$  cm., drop No. 1), and a variation in the

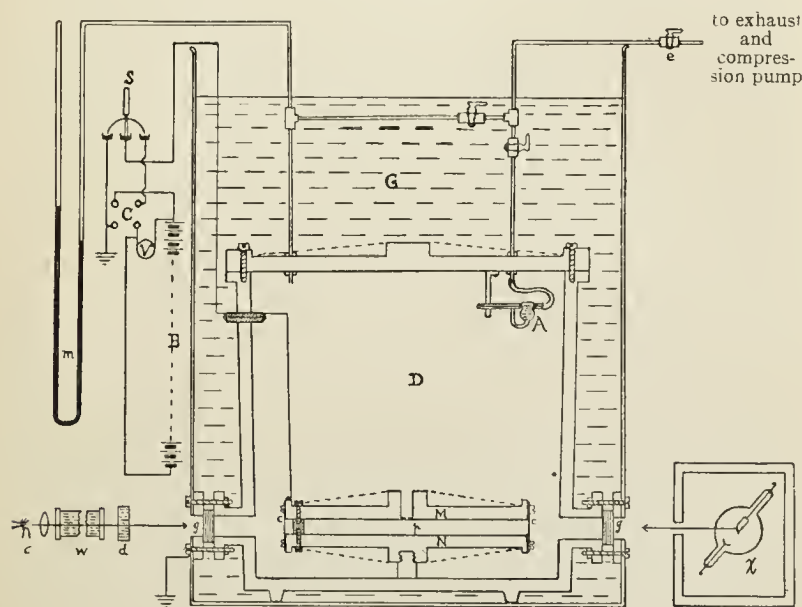


FIG. 7

number of free electrons carried by the drop from 1 on drop No. 28 to 136 on drop No. 56.

The experimental arrangements are shown in Fig. 7. The brass vessel  $D$  was built for work at all pressures up to 15 atmospheres, but since the present observations have to do only with pressures from 76 cm. down, these were measured with a very carefully made mercury manometer  $m$ , which at atmospheric pressure gave precisely

the same reading as a standard barometer. Complete stagnancy of the air between the condenser plates  $M$  and  $N$  was attained, first, by absorbing all of the heat rays from the arc  $A$  by means of a water cell  $w$ , 80 cm. long, and a cupric chloride cell  $d$ , and, secondly, by immersing the whole vessel  $D$  in a constant temperature bath  $G$  of gas-engine oil (40 liters), which permitted, in general, fluctuations of not more than  $.02^{\circ}$  C. during an observation. This constant-temperature bath was found essential if such consistency of measurement as is shown here was to be obtained. A long search for causes of slight irregularity revealed nothing so important as this, and after the bath was installed all of the irregularities vanished. The atomizer  $A$  was blown by means of a puff of carefully dried and dust-free air introduced through cock  $e$ . The air about the drop  $p$  was ionized when desired, or electrons discharged directly from the drop, by means of Röntgen rays from  $X$ , which readily passed through the glass window  $g$ . To the three windows  $g$  (two only are shown) in the brass vessel  $D$  correspond, of course, three windows in the ebonite strip  $c$ , which encircles the condenser plates  $M$  and  $N$ . Through the third of these windows, set at an angle of about  $28^{\circ}$  from the line  $Xpa$  and in the same horizontal plane, the oil drop is observed through a short-focus telescope having a scale in the eyepiece to make possible the exact measurement of the speeds of the droplet-star.

In plotting the actual observations I have used the reciprocal of the pressure  $\frac{1}{p}$  in place of  $l$ , for the reason that  $l$  is a theoretical quantity which is necessarily proportional to  $\frac{1}{p}$ , while  $p$  is the quantity actually measured.

This amounts to writing the correction-term to Stokes's Law in the form  $\left(1 + \frac{b}{pa}\right)$  instead of in the form  $1 + A\frac{l}{a}$  and considering  $b$  the undetermined constant which is to be evaluated, as was  $A$  before, by dividing the slope of our line by its  $y$ -intercept.

Nevertheless, in view of the greater ease of visualization of  $\frac{l}{a}$  all the values of this quantity corresponding to successive values of  $\frac{1}{pa}$  are given in Table IX. Fig. 5 shows the graph obtained by plotting the values of  $e_1$  against  $\frac{1}{pa}$  for the first 51 drops of Table IX, and Fig. 6 shows the extension of this graph to twice as large values of  $\frac{1}{pa}$  and  $e_1$ . It will be seen that there is not the slightest indication of a departure from a linear relation between  $e_1$  and  $\frac{1}{pa}$  up to the value  $\frac{1}{pa} = 620.2$ , which corresponds to a value of  $\frac{l}{a}$  of .4439 (see drop No. 58, Table IX). Furthermore, the scale used in the plotting is such that a point which is one division above or below the line in Fig. 5 represents in the mean an error of 2 in 700. *It will be seen from Figs. 5 and 6 that there is but one drop in the 58 whose departure from the line amounts to as much as 0.5 per cent. It is to be remarked, too, that this is not a selected group of drops, but represents all of the drops experimented upon during 60 consecutive days, during which time the apparatus was taken down several times and set up anew. It is certain, then, that an equation of the form (15) holds very accurately up to*

$\frac{l}{a} = .4$ . The last drop of Fig. 6 seems to indicate the beginning of a departure from this linear relationship. Since such departure has no bearing upon the evaluation of  $e$ , discussion of it will not be entered into here, although it is a matter of great interest for the molecular theory.

Attention may also be called to the completeness of the answers furnished by Figs. 5 and 6 to the question raised in chap. iv as to a possible dependence of the drag which the medium exerts on the drop upon the amount of the latter's charge; also, as to a possible variation of the density of the drop with its radius. Thus drops Nos. 27 and 28 have practically identical values of  $\frac{1}{pa}$ , but while No. 28 carries, during part of the time, but 1 unit of charge (see Table IX), drop No. 27 carries 29 times as much and it has about 7 times as large a diameter. Now, if the small drop were denser than the large one, or if the drag of the medium upon the heavily charged drop were greater than its drag upon the one lightly charged, then for both these reasons drop No. 27 would move more slowly relatively to drop No. 28 than would otherwise be the case, and hence  $e_1$  for drop No. 27 would fall below  $e_1$  for drop No. 28. Instead of this the two  $e_1$  fall so nearly together that it is impossible to represent them on the present scale by two separate dots. Drops Nos. 52 and 56 furnish an even more striking confirmation of the same conclusion, for both drops have about the same value for  $\frac{l}{a}$  and both are exactly on the line, though drop No. 56 carries at one time 68 times as heavy a charge as drop No. 52 and has three times as large a radius. In general, the fact that



Figs. 5 and 6 show no tendency whatever on the part of either the very small or the very large drops to fall above or below the line is experimental proof of the joint correctness of the assumptions of constancy of drop-density and independence of drag of the medium on the charge on the drop.

The values of  $e^{\frac{2}{3}}$  and  $b$  obtained graphically from the  $y$ -intercept and the slope in Fig. 5 are  $e^{\frac{2}{3}} = 61.13 \times 10^{-8}$  and  $b = .000625$ ,  $p$  being measured, for the purposes of Fig. 5 and of this computation in centimeters of Hg at  $23^{\circ}$  C. and  $a$  being measured in centimeters. The value of  $A$  in equations 15 and 16 (p. 101) corresponding to this value of  $b$  is .874.

Instead, however, of taking the result of this graphical evaluation of  $e$ , it is more accurate to reduce each of the observations on  $e_1$  to  $e$  by means of the foregoing value of  $b$  and the equation

$$e^{\frac{2}{3}} \left( 1 + \frac{b}{pa} \right) = e_1^{\frac{2}{3}}$$

The results of this reduction are contained in the last column of Table IX. These results illustrate very clearly the sort of consistency obtained in these observations. *The largest departure from the mean value found anywhere in the table amounts to 0.5 per cent and "the probable error" of the final mean value computed in the usual way is 16 in 61,000.*

Instead, however, of using this final mean value as the most reliable evaluation of  $e$ , it was thought preferable to make a considerable number of observations at atmospheric pressure on drops small enough to make  $t_g$  determinable with great accuracy and yet large enough so that the whole correction term to Stokes's Law

amounted to but a small percentage, since in this case, even though there might be a considerable error in the correction-term constant  $b$ , such error would influence the final value of  $e$  by an inappreciable amount. The first 23 drops of Table IX represent such observations. It will be seen that they show slightly greater consistency than do the remaining drops in the table and that the correction-term reductions for these drops all lie between 1.3 per cent (drop No. 1) and 5.6 per cent (drop No. 23), so that even though  $b$  were in error by as much as 3 per cent (its error is actually not more than 1.5 per cent),  $e$  would be influenced by that fact to the extent of but 0.1 per cent. The mean value of  $e^3$  obtained from the first 23 drops is  $61.12 \times 10^{-8}$ , a number which differs by 1 part in 3,400 from the mean obtained from all the drops.

When correction is made for the fact that the numbers in Table IX were obtained on the basis of the assumption  $\eta = .0001825$ , instead of  $\eta = .0001824$  (see Section II), which was the value of  $\eta_{23}$  chosen in 1913 when this work was first published, the final mean value of  $e^3$  obtained from the first 23 drops is  $61.085 \times 10^{-8}$ . This corresponds to

$$e = 4.774 \times 10^{-10} \text{ electrostatic units.}$$

I have already indicated that as soon as  $e$  is known it becomes possible to find with the same precision which has been attained in its determination the exact number of molecules in a given weight of any substance, the absolute weight of any atom or molecule, the average kinetic energy of agitation of an atom or molecule at any temperature, and a considerable number of other

important molecular and radioactive constants. In addition, it has recently been found that practically all of the important radiation constants like the wave-lengths of X-rays, Planck's  $h$ , the Stefan-Boltzmann constant  $\sigma$ , the Wien constant  $c_2$ , etc., depend for their most reliable evaluation upon the value of  $e$ . In a word,  $e$  is increasingly coming to be regarded, *not only as the most fundamental of physical or chemical constants, but also the one of most supreme importance for the solution of the numerical problems of modern physics*. It seemed worth while, therefore, to drive the method herewith developed for its determination to the limit of its possible precision. Accordingly, in 1914 I built a new condenser having surfaces which were polished optically and made flat to within two wave-lengths of sodium light. These were 22 cm. in diameter and were separated by 3 pieces of echelon plates, 14.9174 mm. thick, and all having optically perfect plane-parallel surfaces. The dimensions of the condenser, therefore, no longer introduced an uncertainty of more than about 1 part in 10,000. The volts were determined after each reading in terms of a Weston standard cell and are uncertain by no more than 1 part in 3,000. The times were obtained from an exceptionally fine printing chronograph built by William Gaertner & Co. It is controlled by a standard astronomical clock and prints directly the time to hundredths of a second. All the other elements of the problem were looked to with a care which was the outgrowth of five years of experience with measurements of this kind. The present form of the apparatus is shown in diagram in Fig. 8, and in Fig. 9 is shown a photograph taken before the enclosing oil tank had been added. This work

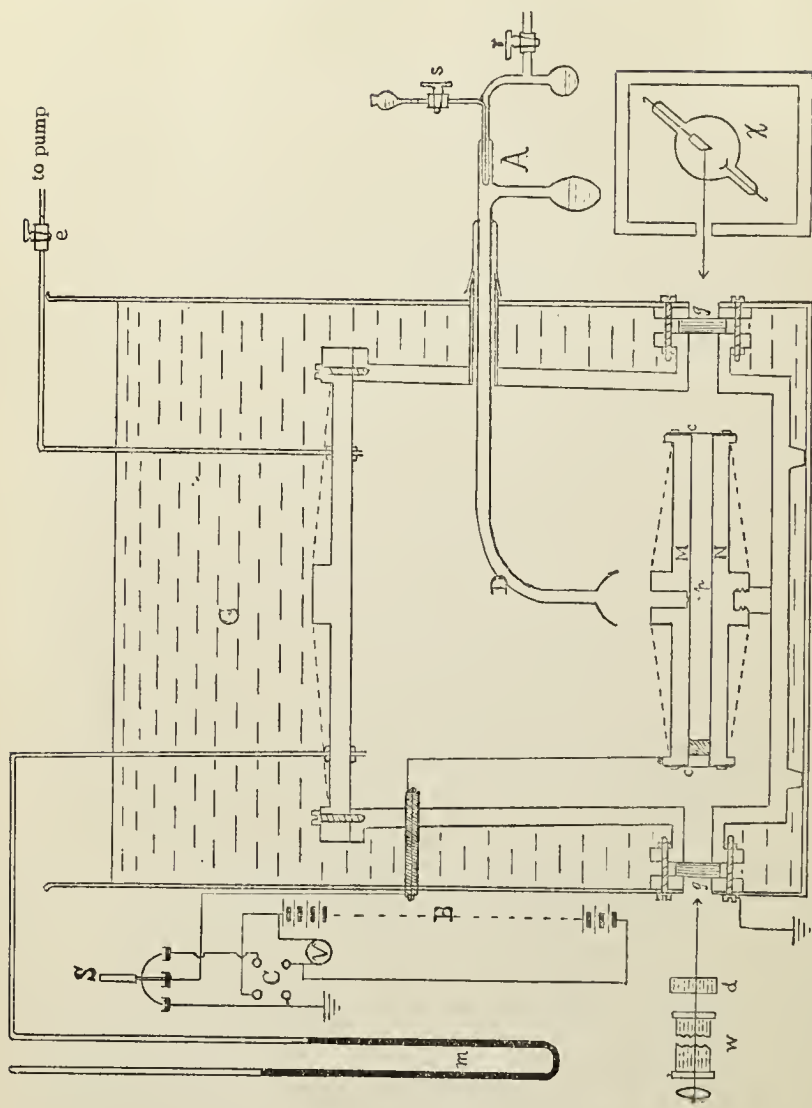


FIG. 8.—4. atomizer through which the oil spray is blown into the cylindrical vessel *D*. *G*, oil tank to keep the temperature constant. *M* and *N*, circular brass plates, electrical field produced by throwing on 10,000-volt battery *B*. Light from arc lamp *a* after heat rays are removed by passage through *w* and *d*, enters chamber through glass window *g* and illuminates droplet *p* between plates *M* and *N* through the pinhole in *M*. Additional ions are produced about *p* by X-rays from the bulb *X*.

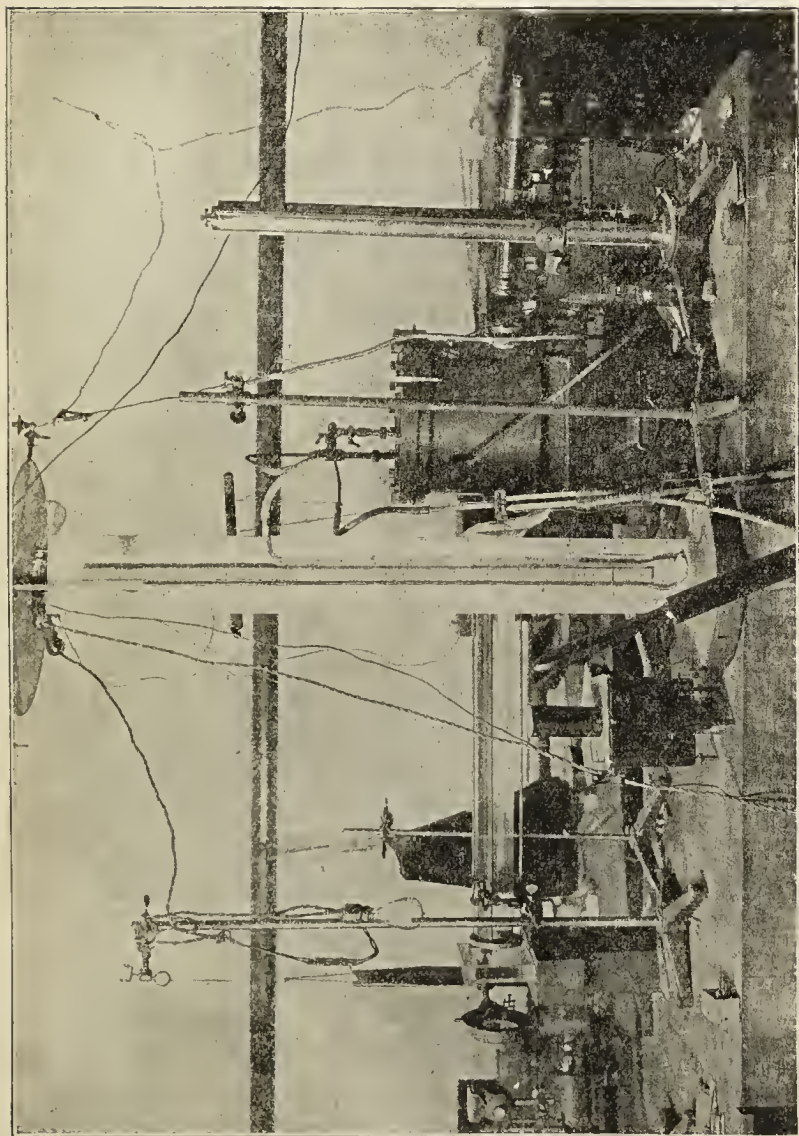


FIG. 9



was concluded in August, 1916, and occupied the better part of two years of time. The final table of results and the corresponding graph are given in Table X and in Fig. 10. The final value of  $e^3$  computed on the basis  $\eta_{23} = .0001824$  is seen to be now  $61.126 \times 10^{-8}$  instead of 61.085, or .07 per cent higher than the value found in 1913. But Dr. Harrington's new value of  $\eta_{23}$ , namely, .00018226, is more reliable than the old value and is lower than it by .07 per cent. Since  $\eta$  appears in the first power in  $e^3$ , it will be seen that the new value<sup>1</sup> of  $e$ , determined with new apparatus and with a completely new determination of all the factors involved, comes out to the fourth place exactly the same as the value published in 1913, namely,

$$e = 4.774 \times 10^{-10} \text{ absolute electrostatic units.}$$

The corresponding values of  $b$  and  $A$  are now .000617 and .863, respectively.

Since the value of the Faraday constant has now been fixed virtually by international agreement<sup>2</sup> at 9,649.4 absolute electromagnetic units, and since this is the number  $N$  of molecules in a gram molecule times the elementary electrical charge, we have

$$\begin{aligned} N \times 4.774 \times 10^{-10} &= 9,649.4 \times 2.9990 \times 10^{-10}, \\ N &= 6.062 \times 10^{20} \end{aligned}$$

Although the probable error in this number computed by the method of least squares from Table X is but one part in 4,000, it would be erroneous to infer that  $e$  and  $N$  are now known with that degree of precision, for there are

<sup>1</sup>For full details see Millikan, *Phil. Mag.*, June, 1917.

<sup>2</sup>At. wt. of Ag. = 107.88; electrochem. eq't. of Ag. = 0.01188. ?  
6,000,000



four constant factors entering into all of the results in Table X and introducing uncertainties as follows: The coefficient of viscosity  $\eta$  which appears in the  $3/2$  power introduces into  $e$  and  $N$  a maximum possible uncertainty of less than 0.1 per cent, say 0.07 per cent. The cross-hair distance which is uniformly duplicatable to one part in two thousand appears in the  $3/2$  power and introduces an uncertainty of no more than 0.07 per cent. All the other factors, such as the volts and the distance between the condenser plates, introduce errors which are negligible in comparison. The uncertainty in  $e$  and  $N$  is then that due to two factors, each of which introduces a maximum possible uncertainty of about 0.07 per cent. Following the usual procedure, we may estimate the uncertainty in  $e$  and  $N$  as the square root of the sum of the squares of these two uncertainties, that is, as about one part in 1000. We have then:

$$e = 4.774 \pm .005 \times 10^{-10}$$

$$N = 6.062 \pm .006 \times 10^{23}$$

Perhaps these numbers have little significance to the general reader who is familiar with no electrical units save those in which his monthly light bills are rendered. If these latter seem excessive, it may be cheering to reflect that the number of electrons contained in the quantity of electricity which courses every second through a common sixteen-candle-power electric-lamp filament, and for which we pay 1/100,000 of 1 cent, is so large that if all the two and one-half million inhabitants of Chicago were to begin to count out these electrons and were to keep on counting them out each at the rate of two a second, and if no one of them were ever to stop to eat, sleep, or die,

TABLE X

No.	Tem. ° C.	P.D. (Volts)	$t_g$ (Sec.)	$v_i$ cm./Sec.	$n$	$a \times 10^4$ cm.	$p$ (cm. Hg)	$\frac{I}{p a}$	$\frac{l}{a}$	$e^{\frac{1}{2}} \times 10^8$	$e^{\frac{3}{2}} \times 10^8$
1.	23.07	6,650	16.50	.06104	7-13	23.40	74.49	57.45	.04111	63.21	61.03
2.	23.00	6,100	16.76	.06099	8-11	23.22	75.00	57.5	.04115	63.204	61.03
3.	23.05	5,308	19.73	.05180	7-15	21.34	74.49	63.0	.04509	63.54	61.16
4.	23.08	4,132	37.82	.02703	4-6	15.33	75.37	80.7	.00205	64.27	60.97
5.	23.06	4,661	40.00	.02521	3-6	14.81	75.00	90.6	.06484	64.63	61.21
6.	23.12	4,111	51.53	.01983	3-4	13.05	75.77	101.3	.00502	63.02	61.19
7.	23.08	5,299	51.46	.01985	2-5	13.05	74.98	102.4	.07329	65.07	61.20
8.	23.01	6,661	50.06	.01823	2-3	12.50	75.40	100.3	.07608	65.13	61.11
9.	23.00	6,082	59.14	.01728	1-4	12.17	75.04	100.7	.07850	65.10	61.05
10.	23.10	4,977	57.46	.01770	3-8	12.34	75.67	107.3	.07680	65.21	61.10
11.	23.13	4,663	16.58	.06165	10-12	22.72	29.20	150.6	.1078	60.70	61.01
12.	23.11	4,661	29.18	.03502	5-7	17.08	30.61	160.1	.1146	67.12	61.07
13.	22.98	4,687	18.81	.05432	8-10	21.26	30.27	155.6	.1114	67.14	61.26
14.	23.12	4,951	47.65	.02145	2-7	13.20	36.80	206.4	.1477	68.00	61.11
15.	23.10	4,648	32.72	.03129	4-6	15.92	31.35	200.7	.1437	68.97	61.39
16.	23.15	3,393	18.34	.05572	12-16	21.11	20.58	227.8	.1030	69.88	61.27
17.	23.12	4,669	40.82	.02294	2-4	13.12	20.10	262.4	.1878	70.85	60.94
18.	23.12	4,691	26.62	.03810	5-7	17.32	20.54	281.4	.2014	71.60	60.98
19.	23.10	3,339	14.10	.07240	15-10	23.00	13.24	321.4	.2297	73.34	61.20
20.	23.14	4,082	30.24	.02665	3-5	14.00	20.72	345.4	.2472	74.27	61.22
21.	23.14	3,350	18.30	.05585	10-13	20.47	13.62	359.1	.2370	74.54	60.97
22.	23.00	3,370	43.88	.02320	3-6	13.17	20.47	371.5	.2659	75.00	60.97
23.	23.13	3,381	46.90	.02170	3-6	12.69	20.74	380.6	.2724	75.62	61.24
24.	23.09	3,345	19.65	.05201	9-12	19.65	13.12	388.5	.2781	75.92	61.24
25.	23.15	3,344	26.70	.03819	0-9	10.57	13.80	438.3	.3137	77.74	61.18

Mean = 61.126.

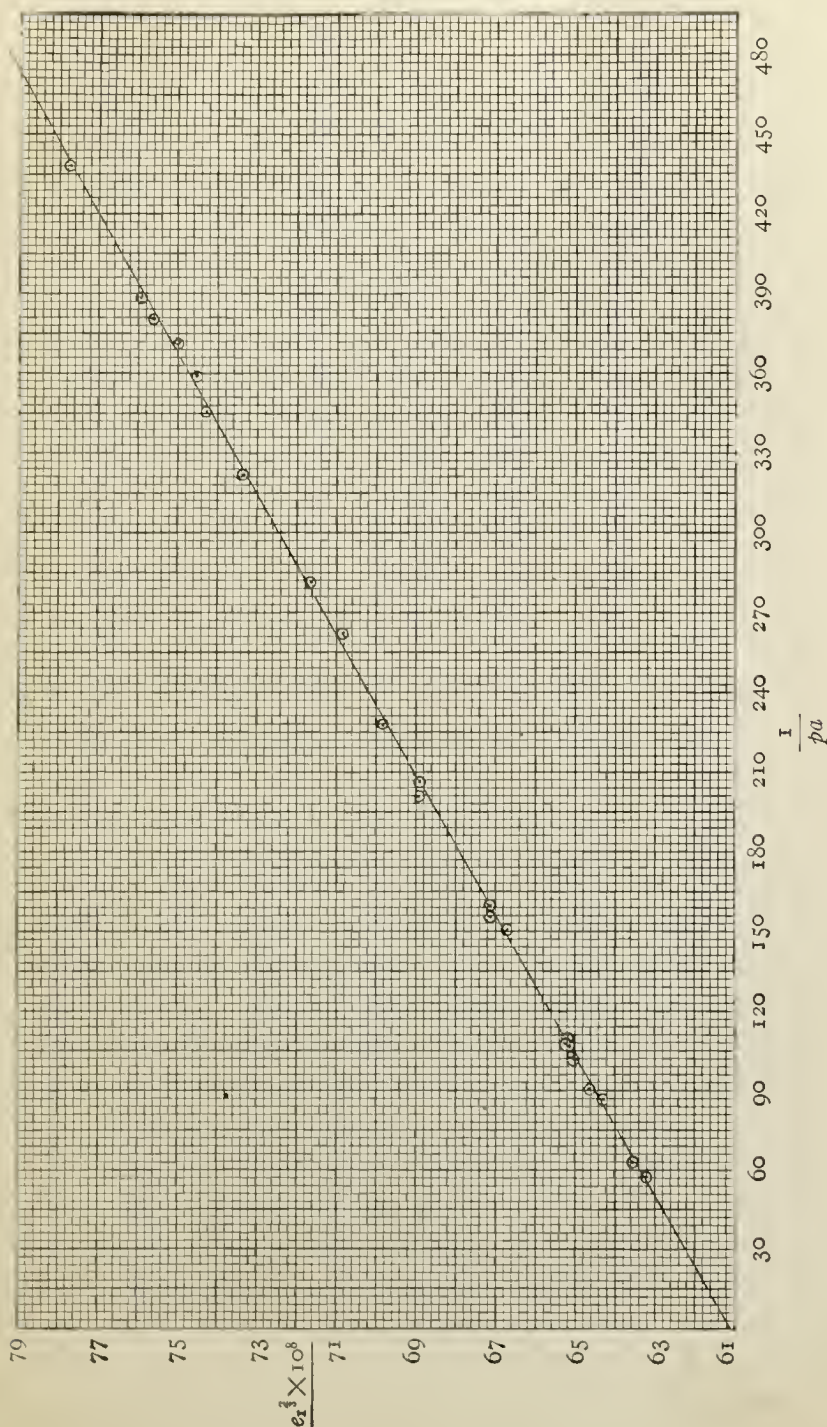


FIG. 10

it would take them just twenty thousand years to finish the task.

Let us now review, with Figs. 5 and 10 before us, the essential elements in the measurement of  $e$ . We discover, first, that electricity is atomic, and we measure the electron in terms of a characteristic speed for each droplet. To reduce these speed units to electrical terms, and thus obtain an absolute value of  $e$ , it is necessary to know how in a given medium and in a given field the speed due to a given charge on a drop is related to the size of the drop. This we know accurately from Stokes's theory and Arnold's experiments when the holes in the medium, that is, when the values of  $\frac{l}{a}$  are negligibly small, but when  $\frac{l}{a}$  is large we know nothing about it. *Consequently there is but one possible way to evaluate  $e$ , namely, to find experimentally how the apparent value of  $e$ , namely,  $e_1$  varies with  $\frac{l}{a}$  or  $\frac{1}{pa}$ , and from the graph of this relation to find what value  $e_1$  approaches as  $\frac{l}{a}$  or  $\frac{1}{pa}$  approaches zero.* So as to get a linear relation we find by analysis that we must plot  $e_1^3$  instead of  $e_1$  against  $\frac{l}{a}$  or  $\frac{1}{pa}$ . We then get  $e$  from the intercept of an experimentally determined straight line on the  $y$ -axis of our diagram. This whole procedure amounts simply to reducing our drop-velocities to what they would be if the pressure were so large or  $\frac{1}{pa}$  so small that the holes in the medium were all closed up. *For this case and for this case alone we know both from Stokes's and Arnold's work exactly the law of motion of the droplet.*

## CHAPTER VI

### THE MECHANISM OF IONIZATION OF GASES BY X-RAYS AND RADIUM RAYS

#### I. EARLY EVIDENCE

Up to the year 1908 the only experiments which threw any light whatever upon the question as to what the act of ionization of a gas consists in were those performed by Townsend<sup>1</sup> in 1900. He had concluded from the theory given on p. 34 and from his measurements on the diffusion coefficients and the mobilities of gaseous ions that both positive and negative ions in gases carry unit charges. This conclusion was drawn from the fact that the value of  $ne$  in the equation  $ne = \frac{v_0 P}{D}$  came out about  $1.23 \times 10^{10}$  electrostatic units, as it does in the electrolysis of hydrogen.

In 1908, however, Townsend<sup>2</sup> devised a method of measuring directly the ratio  $\frac{v_0}{D}$  and revised his original conclusions. His method consisted essentially in driving ions by means of an electric field from the region between two plates  $A$  and  $B$  (Fig. 11), where they had been produced by the direct action of X-rays, through the gauze in  $B$ , and observing what fraction of these ions was driven by a field established between the plates  $B$  and  $C$  to the central disk  $D$  and what fraction drifted by virtue of diffusion to the guard-ring  $C$ .

<sup>1</sup> *Phil. Trans.*, CXCI (1900), 129.

<sup>2</sup> *Proc. Roy. Soc.*, LXXX (1908), 207.



By this method Townsend found that  $ne$  for the negative ions was accurately  $1.23 \times 10^{10}$ , but for the positive ions it was  $2.41 \times 10^{10}$ . From these results the conclusion was drawn that in X-ray ionization *all* of the positive ions are bivalent, i.e., presumably, that the act of ionization by X-rays consists in the detachment from a neutral molecule of two elementary electrical charges.

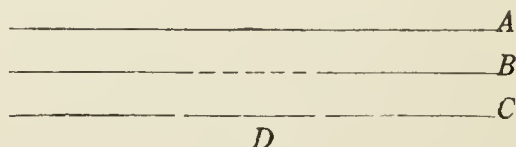


FIG. 11

Townsend accounted for the fact that his early experiments had not shown this high value of  $ne$  for the positive ions by the assumption that by the time the doubly charged positive ions in these experiments had reached the tubes in which  $D$  was measured, most of them had become singly charged through drawing to themselves the singly charged negative ions with which they were mixed. This hypothesis found some justification in the fact that in the early experiments the mean value of  $ne$  for the positive ions had indeed come out some 15 or 20 per cent higher than  $1.23 \times 10^{10}$ —a discrepancy which had at first been regarded as attributable to experimental errors, and which in fact might well be attributed to such errors in view of the discordance between the observations on different gases.

Franck and Westphal,<sup>1</sup> however, in 1909 redetermined  $ne$  by a slight modification of Townsend's original method, measuring both  $v'$  and  $D$  independently, and

<sup>1</sup> *Verh. deutsch. phys. Ges.*, March 5, 1909.



not only found, when the positive and negative ions are separated by means of an electric field so as to render impossible such recombination as Townsend suggested, that  $D$  was of exactly the same value as when they were not so separated, but also that  $ne$  for the positive ions produced by X-rays was but  $1.4 \times 10^{10}$  instead of  $2.41 \times 10^{10}$ . Since this was in fair agreement with Townsend's original mean, the authors concluded that only a small fraction—about 9 per cent—of the positive ions formed by X-rays are doubles, or other multiples, and the rest singles. In their experiments on the ionization produced by  $\alpha$ -rays,  $\beta$ -rays, and  $\gamma$ -rays, they found no evidence for the existence of doubly charged ions.

In summarizing, then, the work of these observers it could only be said that, although both Townsend and Franck and Westphal drew the conclusion that doubly charged ions exist in gases ionized by X-rays, there were such contradictions and uncertainties in their work as to leave the question unsettled. In gases ionized by other agencies than X-rays no one had yet found any evidence for the existence of ions carrying more than a single charge, except in the case of spark discharges from condensers. The spectra of these sparks revealed certain lines called enhanced lines which were thought to be due to doubly ionized atoms. Whether, however, these multiple charges were produced by a single ionizing act or by successive acts was completely unknown.

## II. OIL-DROP EXPERIMENTS ON VALENCY IN GASEOUS IONIZATION

The oil-drop method is capable of furnishing a direct and unmistakable answer to the question as to whether the act of ionization of a gas by X-rays or other agencies

consists in the detachment of one, of several, or of many electrons from a single neutral molecule. For it makes it possible to catch the residue of such a molecule practically at the instant at which it is ionized and to count directly the number of charges carried by that residue. The initial evidence obtained from this method seemed to favor the view that the act of ionization may consist in the detachment of quite a number of electrons from a single molecule, for it was not infrequently observed that a balanced oil drop would remain for several seconds unchanged in charge while X-rays were passing between the plates, and would then suddenly assume a speed which corresponded to a change of quite a number of electrons in its charge.

It was of course recognized from the first, however, that it is very difficult to distinguish between the practically simultaneous advent upon a drop of two or three separate ions and the advent of a doubly or trebly charged ion, but a consideration of the frequency with which ions were being caught in the experiments under consideration, a change occurring only once in, say, 10 seconds, seemed at first to render it improbable that the few double, or treble, or quadruple catches observed when the field was on could represent the simultaneous advent of separate ions. It was obvious, however, that the question could be conclusively settled by working with smaller and smaller drops. For the proportion of double or treble to single catches made in a field of strength between 1,000 and 6,000 volts per centimeter should be independent of the size of the drops if the doubles are due to the advent of doubly charged ions, while this proportion should decrease with the square of the radius

of the drop if the doubles are due to the simultaneous capture of separate ions.

Accordingly, Mr. Harvey Fletcher and the author,<sup>1</sup> suspended, by the method detailed in the preceding chapter, a very small positively charged drop in the upper part of the field between  $M$  and  $N$  (Fig. 12), adjusting either the charge upon the drop or the field strength until the drop was nearly balanced. We then produced beneath the drop a sheet of X-ray ionization. With the arrangement shown in the figure, in which  $M$

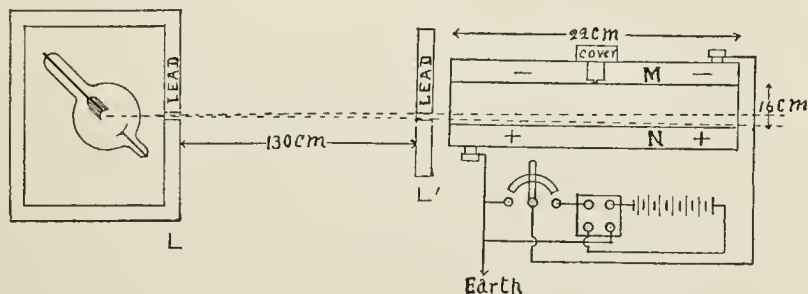


FIG. 12

and  $N$  are the plates of the condenser previously described, and  $L$  and  $L'$  are thick lead screens, the positive ions are thrown, practically at the instant of formation, to the upper plate. When one of them strikes the drop it increases the positive charge upon it, and the amount of the charge added by the ion to the drop can be computed from the observed change in the speed of the drop.

For the sake of convenience in the measurement of successive speeds a scale containing 70 equal divisions was placed in the eyepiece of the observing cathetometer telescope, which in these experiments produced a

<sup>1</sup> *Phil. Mag.*, XXIII (1911), 753.

magnification of about 15 diameters. The method of procedure was, in general, first, to get the drop nearly balanced by shaking off its initial charge by holding a little radium near the observing chamber, then, with a switch, to throw on the X-rays until a sudden start in the drop revealed the fact that an ion had been caught, then to throw off the rays and take the time required for it to move over 10 divisions, then to throw on the rays until another sudden quickening in speed indicated the capture of another ion, then to measure this speed and to proceed in this way without throwing off the field at all until the drop got too close to the upper plate, when the rays were thrown off and the drop allowed to fall under gravity to the desired distance from the upper plate. In order to remove the excess of positive charge which the drop now had because of its recent captures, some radium was brought near the chamber and the field thrown off for a small fraction of a second. As explained in preceding chapters, ions are caught by the drop many times more rapidly when the field is off than when it is on. Hence it was in general an easy matter to bring the positively charged drop back to its balanced condition, or indeed to any one of the small number of working speeds which it was capable of having, and then to repeat the series of catches described above. In this way we kept the same drop under observation for hours at a time, and in one instance we recorded 100 successive captures of ions by a given drop, and determined in each case whether the ion captured carried a single or a multiple charge.

The process of making this determination is exceedingly simple and very reliable. For, since electricity is

atomic in structure, there are only, for example, three possible speeds which a drop can have when it carries 1, 2, or 3 elementary charges, and it is a perfectly simple matter to adjust conditions so that these speeds are of such different values that each one can be recognized unfaillingly even without a stop-watch measurement. Indeed, the fact that electricity is atomic is in no way more beautifully shown than by the way in which, as reflected in Table XI, these relatively few possible working speeds recur. After all the possible speeds have been located it is only necessary to see whether one of them is ever skipped in the capture of a new ion in order to know whether or not that ion was a double. Table XI represents the results of experiments made with very hard X-rays produced by means of a powerful 12-inch Scheidel coil, a mercury-jet interrupter, and a Scheidel tube whose equivalent spark-length was about 5 inches. No attempt was made in these experiments to make precise determinations of speed, since a high degree of accuracy of measurement was not necessary for the purpose for which the investigation was undertaken. Table XI is a good illustration of the character of the observations. The time of the fall under gravity recorded in the column headed " $t_g$ " varies slightly, both because of observational errors and because of Brownian movements. Under the column headed " $t_f$ " are recorded the various observed values of the times of rise through 10 divisions of the scale in the eyepiece. A star (\*) after an observation in this column signifies that the drop was moving with gravity instead of against it. The procedure was in general to start with the drop either altogether neutral (so that it fell when the field was on

with the same speed as when the field was off), or having one single positive charge, and then to throw on positive

TABLE XI

Plate Distance 1.6 cm. Distance of Fall .0975 cm. Volts 1,015.

Temperature 23° C. Radius of Drop .000063 cm.

$t_g$	$t_F$	No. of Charges on Drop	No. of Charges on Ion Caught	$t_g$	$t_F$	No. of Charges on Drop	No. of Charges on Ion Caught
19.0	100.0	1 P		20.0	10.0*	1 N	
	16.0	2 P	1 P		20.0*	0	1 P
	8.0	3 P	1 P		100.0	1 P	1 P
20.0					20.0*	0	1 N
	16.0	2 P			100.0	1 P	1 P
	8.0	3 P	1 P		16.0	2 P	1 P
					8.0	3 P	1 P
	100.0	1 P					
	17.0	2 P	1 P		104.0	1 P	
	8.2	3 P	1 P		15.0	2 P	1 P
	6.0	4 P	1 P		9.0	3 P	1 P
					6.0	4 P	
	7.0*	2 N	1 P		6.5*	2 N	
	9.8*	1 N	1 N		10.0*	1 N	1 P
	7.0*	2 N			20.0*	0	1 P
21.0	20.0*	0			100.0	1 P	1 P
	95.0	1 P	1 P		15.5	2 P	1 P
	16.5	2 P	1 P		8.0	3 P	1 P
	8.0	3 P	1 P		6.0	4 P	
	6.0	4 P					
					100.0	1 P	
	100.0	1 P	1 P		16.5	2 P	1 P
	16.0	2 P	1 P				
	8.4	3 P			20.0*	0	1 P
					100.0	1 P	1 P
20.0	106.0	1 P			16.6	2 P	1 P
	16.0	2 P	1 P		8.8	3 P	1 P
	8.4	3 P	1 P		5.7	4 P	1 P
	10.0*	1 N			100.0	1 P	
	20.0*	0	1 P		20.0*	0	1 N
			1 P		10.0*	1 N	1 N
	100.0	1 P	1 P		20.0*	0	1 P
	16.0	2 P					
					44 catches, all singles		
	100.0	1 P	1 P				
	16.0	2 P	1 P				
	8.0	3 P					



charges until its speed came to the 6.0 second value, then to make it neutral again with the aid of radium, and to begin over again.

It will be seen from Table XI that in 4 cases out of 44 we caught negatives, although it would appear from the arrangement shown in Fig. 12 that we could catch only positives. These negatives are doubtless due to secondary rays which radiate in all directions from the air molecules when these are subjected to the primary X-ray radiation.

Toward the end of Table XI is an interesting series of catches. At the beginning of this series, the drop was charged with 2 negatives which produced a speed in the direction of gravity of 6.5 seconds. It caught in succession 6 single positives before the field was thrown off. The corresponding times were 6.5\*, 10\*, 20\*, 100, 15.5, 8.0, 6.0. The mean time during which the X-rays had to be on in order to produce a "catch" was in these experiments about six seconds, though in some instances it was as much as a minute. The majority of the times recorded in column  $t_F$  were actually measured with a stop watch as recorded, but since there could be no possibility of mistaking the 100-second speed, it was observed only four or five times. It will be seen from Table XI that out of 44 catches of ions produced by very hard X-rays there is not a single double. As a result of observing from 500 to 1,000 catches in the manner illustrated in Table XI, we came to the conclusion that, although we had entered upon the investigation with the expectation of proving the existence of valency in gaseous ionization, *we had instead obtained direct, unmistakable evidence that the act of ionization of air*

*molecules by both primary and secondary X-rays of widely varying degrees of hardness, as well as by  $\beta$ - and  $\gamma$ -rays, uniformly consists, under all the conditions which we were able to investigate, in the detachment from a neutral molecule of one single elementary electrical charge.*

### III. RECENT EVIDENCE AS TO NATURE OF IONIZATION PRODUCED BY ETHER WAVES

Although Townsend and Franck and Westphal dissented from the foregoing conclusion, all the evidence which has appeared since has tended to confirm it. Thus Salles,<sup>1</sup> using a new method due to Langevin of measuring directly the ratio  $\left(\frac{v_0}{D}\right)$  of the mobility to the diffusion coefficient, concluded that when the ionization is produced by  $\gamma$ -rays there are no ions bearing multiple charges. Again, the very remarkable photographs (see plate opposite p. 190) taken by C. T. R. Wilson in the Cavendish Laboratory of the tracks made by the passage of X-rays through gases show no indication of a larger number of negatively than of positively charged droplets. Such an excess is to be expected if the act of ionization ever consists in these experiments in the detachment of two or more negative electrons from a neutral molecule. Further, if the initial act of ionization by X-rays ever consists in the ejection of two or more corpuscles from a single atom, there should appear in these Wilson photographs a rosette consisting of a group of zigzag lines starting from a common point. A glance at the plate opposite p. 192 shows that this is not the case, each zigzag line having its own individual starting-point.

<sup>1</sup> *Le Radium*, X (1913), 113, 119.

There are two other types of experiments which throw light on this question.

When in the droplet experiments the X-rays are allowed to fall directly upon the droplet, we have seen that they detach negative electrons from it, and if the gas is at so low a pressure that there is very little chance of the capture of ions by the droplet, practically all of its changes in charge have this cause. Changes produced under these conditions appear, so far as I have yet been able to discover, to be uniformly unit changes. Also, when the changes are produced by the incidence on the droplet of ultra-violet light, so far as the experiments which have been carried out by myself or my pupils go, they usually, though not always, have appeared to correspond to the loss of one single electron. The same seems to have been true in the experiments reported by A. Joffé,<sup>1</sup> who has given this subject careful study.

Meyer and Gerlach,<sup>2</sup> it is true, seem very often to observe changes corresponding to the simultaneous loss of several electrons. It is to be noted, however, that their drops are generally quite heavily charged, carrying from 10 to 30 electrons. Under such conditions the loss of a single electron makes but a minute change in speed, and is therefore likely not only to be unnoticed, but to be almost impossible to detect *until the change has become more pronounced through the loss of several electrons. This question, then, can be studied reliably only when the field is powerful enough to hold the droplet balanced with only one or two free electrons upon it.* Experiments made under such conditions with my apparatus by both Derieux<sup>3</sup> and

<sup>1</sup> *Sitzungsber. d. k. Bayerischen Akad. d. Wiss.* (1913), p. 19.

<sup>2</sup> *Ann. d. Phys.*, XLV, 177; XLVII, 227. <sup>3</sup> *Phys. Rev.*, X (1918), 283.

Kelly<sup>1</sup> show quite conclusively that the act of photo-emission under the influence of ultra-violet light consists in the ejection of a single electron at each emission.

Table XII contains one series of observations of this sort taken with my apparatus by Mr. P. I. Pierson. The first column gives the volts applied to the plates of the condenser shown in Fig. 7, p. 111. These were made variable so that the drop might always be pulled up with a slow speed even though its positive charge were continually increasing. The second and third columns give the times required to move 1 cm. under gravity and under the field respectively. The fourth column gives the time intervals required for the drop to experience a change in charge under the influence of a constant source of ultra-violet light—a quartz mercury lamp. The fifth column gives the total charge carried by the drop computed from equation (12), p. 91. The sixth column shows the change in charge computed from equation (10), p. 70. This is seen to be as nearly a constant as could be expected in view of Brownian movements and the inexact measurements of volts and times. The mean value of  $e_1$  is seen to be  $5.1 \times 10^{-10}$ , which yields with the aid of equation (16), p. 101, after the value of  $A$  found for oil drops has been inserted,  $e = 4.77 \times 10^{-10}$ , which is in better agreement with the result obtained with oil drops than we had any right to expect. In these experiments the light was weak so that the changes come only after an average interval of 29 seconds and it will be seen that *they are all unit changes*.

So long, then, as we are considering the ionization of neutral atoms through the absorption of an ether wave

<sup>1</sup> *Phys. Rev.*, XVI (1920), 260.

of any kind, the evidence at present available indicates that the act always consists in the detachment from the

TABLE XII

MERCURY DROPLET OF RADIUS  $a = 8 \times 10^{-5}$  CM. DISCHARGING ELECTRONS UNDER THE INFLUENCE OF ULTRA-VIOLET LIGHT

Volts	Drop No. 1 $t_g$ Sec. per Cm.	$F$ Sec. per Cm.	Time Interval between Discharges in Seconds	$e_n \times 10^{10}$	Change in $\epsilon$	No Electrons Emitted
2,260.....	11.0	- 1200	11	{ 49.4 50.5 }	4.4	1
3,070.....	11.0	+ 32.8				
1,960. ....	11.0	- 194.	12.8	54.4	6.4	1
1,960.....		+ 190	23	60.8	4.2	1
1,820.....	11.2	+ 220	40	65.0	4.8	1
1,690.....		+ 230	15.2	69.8	5.3	1
1,550 ....		+ 332		75.1		
3,040 ....	Drop No. 2 10.4	+ 98	5.6	43.5		
2,540.....		+ 200	18.6	49.4	5.9	1
2,230.....		+ 300	35.0	55.2	5.5	1
2,230.....		+ 76	42	60.7	4.3	1
1,930.....		+ 200	54	65.0	4.6	1
1,810.....		+ 176	70	69.6	5.6	1
1,650.....		+ 250	45	75.2	4.2	1
1,520.....		+ 500	9.8	79.4	5.5	1
1,520.....		119		85.1		
		Mean....	29	Mean..	5.1	

atom of one single negative electron, the energy with which this electron is ejected from the atom depending, as

we shall see in chap. x, in a very definite and simple way upon the frequency of the ether wave which ejects it.

#### IV. IONIZATION BY $\beta$ -RAYS

When the ionization is due to the passage of  $\beta$ -rays through matter, the evidence of the oil-drop experiments as well as that of C. T. R. Wilson's experiments (see chap. ix) on the photographing of the tracks of the  $\beta$ -rays is that here, too, the act consists in the detachment of one single electron from a single atom. This experimental result is easy to understand in the case of the  $\beta$ -rays, when it is remembered that Wilson's photographs prove directly the fact, long known from other types of evidence, that a  $\beta$ -ray, in general, ionizes but a very minute fraction of the number of atoms through which it shoots before its energy is expended. If, then, its chance, in shooting through an atom, of coming near enough to one of the electronic constituents of that atom to knock it out is only one in one thousand, or one in one million, then its chance of getting near enough to two electronic constituents of the same atom to knock them both out is likely to be negligibly small. The argument here rests, however, on the assumption that the electrons within the atom are independent of one another, which is not necessarily the case, so that the matter must be decided after all solely by experiment.

The difference between the act of ionization when produced by a  $\beta$ -ray and when produced by an ether wave seems, then, to consist wholly in the difference in the energy with which the two agencies hurl the electron from its mother atom. Wilson's photographs show that  $\beta$ -rays do not eject electrons from atoms with appre-



ciable speeds, while ether waves may eject them with tremendous energy. Some of Wilson's photographs showing the effect of passing X-rays through air are shown in the most interesting plate opposite p. 190. The original X-rays have ejected electrons with great speeds from a certain few of the atoms of the gas, and it is the tracks of these electrons as they shoot through the atoms of the gas, ionizing here and there as they go, which constitute the wiggly lines shown in the photograph. Most of the ionization, then, which is produced by X-rays is a secondary effect due to the negative electrons, i.e., the  $\beta$ -rays which the X-rays eject. If these  $\beta$ -rays could in turn eject electrons with ionizing speeds, each of the dots in one of these  $\beta$ -ray tracks would be the starting-point of a new wiggly line like the original one. But such is not the case. We may think, then, of the  $\beta$ -rays as simply shaking loose electronic dust from some of the atoms through which they pass while we think of the X-rays as taking hold in some way of the negative electrons within an atom and hurling them out with enormous energy.

#### V. IONIZATION BY $\alpha$ -RAYS

But what happens to the electronic constituents of an atom when an  $\alpha$ -particle, that is, a helium atom, shoots through it? Some of Bragg's experiments and Wilson's photographs show that the  $\alpha$ -particles shoot in straight lines through from 3 to 7 cm. of air before they are brought to rest. We must conclude, then, that an atom has so loose a structure that another atom, *if endowed with enough speed*, can shoot straight through it without doing anything more than, in some instances, to

shake off from that atom an electron or two. The tracks shown in Figs. 14 and 15, facing p. 190, are Wilson's photographs of the tracks of the  $\alpha$ -particles of radium. They ionize so many of the atoms through which they pass that the individual droplets of water which form about the ions produced along the path of the ray, and which are the objects really photographed, are not distinguishable as individuals. The sharp changes in the direction of the ray toward the end of the path are convincing evidence that the  $\alpha$ -particle actually goes through the atoms instead of pushing them aside as does a bullet. For if one solar system, for example, endowed with a stupendous speed, were to shoot straight through another similar system, but without an actual impact of their central bodies, the deflection from its straight path which the first system experienced might be negligibly small *if its speed were high enough*, and that for the simple reason that the two systems would not be in each other's vicinity long enough to produce a deflecting effect. In technical terms the time integral of the force would be negligibly small. The slower the speed, however, the longer this time, and hence the greater the deflection. Thus it is only when the  $\alpha$ -particle shown in Fig. 15 has lost most of its velocity—i.e., it is only toward the end of its path—that the nuclei of the atoms through which it passes are able to deflect it from its straight path. If it pushed the molecules aside as a bullet does, instead of going through them, the resistance to its motion would be greatest when the speed is highest. Now, the facts are just the opposite of this. The  $\alpha$ -particle ionizes several times more violently toward the end of its path than toward the beginning, and it therefore loses energy

more rapidly when it is going slowly than when it is going rapidly. Further, it is deflected more readily, then, as the photograph shows. All of this is just as it should be if the  $\alpha$ -particle shoots straight through the molecules in its path instead of pushing them aside.

These photographs of Wilson's are then the most convincing evidence that we have that the atom is a sort of miniature stellar system with constituents which are unquestionably just as minute with respect to the total volume occupied by the atom as are the sun and planets and other constituents of the solar system with respect to the whole volume inclosed within the confines of this system. When two molecules of a gas are going as slowly as they are in the ordinary motion of thermal agitation, say a mile a second, when their centers come to within a certain distance—about  $0.2 \mu\mu$  (millionths of a millimeter)—they repel one another and so the two systems do not interpenetrate. This is the case of an ordinary molecular collision. But endow one of these molecules with a large enough energy and it will shoot right through the other, sometimes doubtless without so much as knocking out a single electron. This is the case of an  $\alpha$ -particle shooting through air.

But the question to which we are here seeking an answer is, does an individual  $\alpha$ -particle ever knock more than one electron from a single atom or molecule through which it passes, so as to leave that atom doubly or trebly charged? The oil-drop method used at low pressures<sup>1</sup> has given a very definite answer to this question. *In no gas or vapor except helium, which we have as yet tried, is there any certain evidence that an individual  $\alpha$ -ray in*

<sup>1</sup> *Rays of Positive Electricity* (1913), p. 46.

*shooting through an atom is able to remove from that atom more than one single electron at a time.*

The foregoing result has been obtained by shooting the  $\alpha$ -rays from polonium through a rarefied gas in an oil-drop apparatus of the type sketched in Fig. 12, catching upon a balanced oil drop the positively charged residue of one of the atoms thus ionized, and counting, by the change in speed imparted to the droplet, the number of electrons which were detached from the captured atom by the passage of the  $\alpha$ -ray through or near it.<sup>1</sup>

This mode of experimenting extended to helium, however, has yielded the most interesting result<sup>2</sup> that every sixth one on the average of all the passages, or "shots," which detached any electrons at all from the helium atom detached both of the two electrons which the neutral helium atom possesses. Since some of the ionization produced along the path of an  $\alpha$ -ray is probably due to slow-speed secondary  $\beta$ -rays produced by the  $\alpha$ -ray, it is probable that the fraction of the actual passages through helium atoms of  $\alpha$ -rays themselves which detach both electrons is greater than the foregoing one in six. It has been estimated by Fowler at as high as three in four.

The foregoing experimental result of one in six was obtained only at the very end of the range of the  $\alpha$ -rays where they have their maximum ionizing power. When these rays were near the beginning of their range, and therefore were moving much more rapidly, the fraction of the number of double catches to total catches was only about half as much, i.e., *the chance of getting both electrons*

<sup>1</sup> Millikan, Gottschalk, and Kelly, *Phys. Rev.*, XI (1920), 157.

<sup>2</sup> Millikan, *Phys. Rev.*, XVIII (1921), 456. Wilkins, *ibid.*, XXIV (1922), 210.

*at a single shot is much smaller with a high-speed bullet than with a slow-speed one.* This is to be expected if the two electrons are independent of each other, i.e., if the removal of one does not carry the other out with it.

The foregoing is, I think, the only experiment which has yet been devised in which the act of ionization is isolated and studied as an individual thing.

Since 1913, however, very definite evidence has come in from two different sources that multiply-valent ions are often produced in discharge tubes. The most unambiguous proof of this result has been furnished by the spectroscope. Indeed, Mr. Bowen and the author have recently found with great definiteness that high-voltage vacuum sparks give rise to spectral lines which are due to singly-, doubly-, trebly-, quadruply-, and quintuply-charged atoms of the elements from lithium to nitrogen, and even to sextuply-charged ones in the case of sulphur.<sup>1</sup> In view of the foregoing studies with X-rays,  $\beta$ -rays, and  $\alpha$ -rays, it is probable that these spectroscopically discovered multiply-charged ions are produced by successive ionizations such as might be expected to take place in a region carrying a very dense electron current, such as must exist in our "hot-sparks."

Again, J. J. Thomson has brought forward evidence<sup>2</sup> that the positive residues of atoms which shoot through discharge tubes in a direction opposite to that of the cathode rays have suffered multiple ionization. Indeed, he thinks he has evidence that the act of ionization of atoms of mercury consists either in the detachment of one negative electron or else in the detachment of eight.

<sup>1</sup> *Phys. Rev.*, September or October, 1924.

<sup>2</sup> *Rays of Positive Electricity* (1913), p. 46.

His evidence for the existence in the case of mercury of multiple charges from one up to eight is certainly very convincing, and it is possible, also, that under his conditions the act of ionization itself may consist in the detachment either of one or of eight electrons as he suggests. Further evidence upon this point must be sought.

## VI. SUMMARY

The results of the studies reviewed in this chapter may be summarized thus:

1. The act of ionization by  $\beta$ -rays seems to consist in the shaking off without any appreciable energy of one single electron from an occasional molecule through which the  $\beta$ -ray passes. The faster the  $\beta$ -ray the less frequently does it ionize.

2. The act of ionization by ether waves, i.e., by X-rays or light, seems to consist in the hurling out with an energy which may be very large, but which depends upon the frequency of the incident ether wave, of one single electron from an occasional molecule over which this wave passes.

3. The act of ionization by rapidly moving  $\alpha$ -particles consists generally in the shaking loose of one single electron from the atom through which it passes, though in the case of helium, two electrons are certainly sometimes removed at once. It may be, too, that a very slow-moving positive ray, such as J. J. Thomson used, may detach several electrons from a single atom.



## CHAPTER VII

### BROWNIAN MOVEMENTS IN GASES

#### I. HISTORICAL SUMMARY

In 1827 the English botanist, Robert Brown, first made mention of the fact that minute particles of dead matter in suspension in liquids can be seen in a high-power microscope to be endowed with irregular wiggling motions which strongly suggest "life."<sup>1</sup> Although this phenomenon was studied by numerous observers and became known as the phenomenon of the Brownian movements, it remained wholly unexplained for just fifty years. The first man to suggest that these motions were due to the continual bombardment to which these particles are subjected because of the motion of thermal agitation of the molecules of the surrounding medium was the Belgian Carbonelle, whose work was first published by his collaborator, Thirion, in 1880,<sup>2</sup> although three years earlier Delsaulx<sup>3</sup> had given expression to views of this sort but had credited Carbonelle with priority in adopting them. In 1881 Bodoszewski<sup>4</sup> studied the Brownian movements of smoke particles and other suspensions *in air* and saw in them "an approximate image of the movements of the gas molecules as postulated by the kinetic theory of gases." Others, notably Gouy,<sup>5</sup>

<sup>1</sup> *Phil. Mag.*, IV (1828), 161.

<sup>2</sup> *Revue des questions scientifiques*, Louvain, VII (1880), 5.

<sup>3</sup> *Ibid.*, II (1877), 319.

<sup>4</sup> *Dinglers polyt. Jour.*, CCXXXIX (1881), 325.

<sup>5</sup> *Jour. de Phys.*, VII (1888), 561; *Comptes rendus*, CIX (1889), 102.

urged during the next twenty years the same interpretation, but it was not until 1905 that a way was found to subject the hypothesis to a quantitative test. Such a test became possible through the brilliant theoretical work of Einstein<sup>1</sup> of Bern, Switzerland, who, starting merely with the assumption that the mean kinetic energy of agitation of a particle suspended in a fluid medium must be the same as the mean kinetic energy of agitation of a gas molecule at the same temperature, developed by unimpeachable analysis an expression for the mean distance through which such a particle should drift in a given time through a given medium because of this motion of agitation. This distance could be directly observed and compared with the theoretical value. Thus, suppose one of the wiggling particles is observed in a microscope and its position noted on a scale in the eyepiece at a particular instant, then noted again at the end of  $\tau$  (for example, 10) seconds, and the displacement  $\Delta x$  in that time along one particular axis recorded. Suppose a large number of such displacements  $\Delta x$  in intervals all of length  $\tau$  are observed, each one of them squared, and the mean of these squares taken and denoted by  $\overline{\Delta x^2}$ : Einstein showed that the theoretical value of  $\overline{\Delta x^2}$  should be

$$\overline{\Delta x^2} = \frac{2RT}{NK} \tau \dots\dots\dots (21)$$

in which  $R$  is the universal gas constant per gram molecule, namely,  $831.5 \times 10^5 \frac{\text{ergs}}{\text{degrees}}$ ,  $T$  the temperature on the absolute scale,  $N$  the number of molecules in one gram molecule, and  $K$  a resistance factor depending

<sup>1</sup> *Ann. d. Phys.* (4), XVII (1905), 549; XIX (1906), 371; XXII (1907), 569.

upon the viscosity of the medium and the size of the drop, and representing the ratio between the force applied to the particle in any way and the velocity produced by that force. If Stokes's Law, namely,  $F = 6\pi\eta av$ , held for the motion of the particle through the medium, then  $K = \frac{F}{v}$  would have the value  $6\pi\eta a$ , so that Einstein's formula would become

$$\overline{\Delta x^2} = \frac{RT}{N3\pi\eta a} \tau \dots\dots\dots (22)$$

This was the form which Einstein originally gave to his equation, a very simple derivation of which has been given by Langevin.<sup>1</sup> The essential elements of this derivation will be found in Appendix C.

The first careful test of this equation was made on suspensions in liquids by Perrin,<sup>2</sup> who used it for finding  $N$  the number of molecules in a gram molecule. He obtained the mean value  $N = 68.2 \times 10^{22}$ , which, in view of the uncertainties in the measurement of both  $K$  and  $\overline{\Delta x^2}$ , may be considered as proving the correctness of Einstein's equation within the limits of error of Perrin's measurements, which differ among themselves by as much as 30 per cent.

## II. QUANTITATIVE MEASUREMENTS IN GASES

Up to 1909 there had been no quantitative work whatever on Brownian movements in gases. Bodoszewski had described them fully and interpreted them correctly

<sup>1</sup> *Comptes rendus*, CXLVI (1908), 530.

<sup>2</sup> *Ibid.*, p. 967; CXLVII (1908), 475, 530, 594; CLII (1911), 1380, 1569; see also Perrin, *Brownian Movements and Molecular Reality*, Engl. tr. by Soddy, 1912.

in 1881. In 1906 Smoluchowski<sup>1</sup> had computed how large the mean displacements in air for particles of radius  $a=10^{-4}$  ought to be, and in 1907 Ehrenhaft<sup>2</sup> had recorded displacements of the computed order with particles the sizes of which he made, however, no attempt to measure, so that he knew nothing at all about the resistance factor  $K$ . There was then nothing essentially quantitative about this work.

In March, 1908, De Broglie, in Paris,<sup>3</sup> made the following significant advance. He drew the metallic dust arising from the condensation of the vapors coming from an electric arc or spark between metal electrodes (a phenomenon discovered by Hemsalech and De Watterville<sup>4</sup>) into a glass box and looked down into it through a microscope upon the particles rendered visible by a beam of light passing horizontally through the box and illuminating thus the Brownian particles in the focal plane of the objective. His addition consisted in placing two parallel metal plates in vertical planes, one on either side of the particles, and in noting that upon applying a potential difference to these plates some of the particles moved under the influence of the field toward one plate, some remained at rest, while others moved toward the other plate, thus showing that a part of these particles were positively electrically charged and a part negatively. In this paper he promised a study of the charges on these particles. In May, 1909, in fulfilling this promise<sup>5</sup> he

<sup>1</sup> *Ann. der Phys.*, IV (1906), 21, 756.

<sup>2</sup> *Wiener Berichte*, CXVI (1907), II, 1175.

<sup>3</sup> *Comptes rendus*, CXLVI (1908), 624, 1010.

<sup>4</sup> *Ibid.*, CXLIV (1907), 1338.

<sup>5</sup> *Ibid.*, CXLVIII (1909), 1316.

made the first quantitative study of Brownian movements in gases. The particles used were minute droplets of water condensed upon tobacco smoke. The average rate at which these droplets moved in Broglie's horizontal electric field was determined. The equation for this motion was

$$F_e = Kv \dots\dots\dots (23)$$

The mean  $\overline{\Delta x^2}$  was next measured for a great many particles and introduced into Einstein's equation:

$$\overline{\Delta x^2} = \frac{2RT}{NK} \tau.$$

From these two equations  $K$  was eliminated and  $e$  obtained in terms of  $N$ . Introducing Perrin's value of  $N$ , De Broglie obtained from one series of measurements  $e = 4.5 \times 10^{-10}$ ; from another series on larger particles he got a mean value several times larger—a result which he interpreted as indicating multiple charges on the larger particles. Although these results represent merely mean values for many drops which are not necessarily all alike, either in radius or charge, yet they may be considered as the first experimental evidence that Einstein's equation holds approximately, in gases, and they are the more significant because nothing has to be assumed about the size of the particles, if they are all alike in charge and radius, or about the validity of Stokes's Law in gases, the  $K$ -factor being eliminated.

The development of the oil-drop method made it possible to subject the Brownian-movement theory to a more accurate and convincing experimental test than had heretofore been attainable, and that for the following reasons:

1. It made it possible to hold, with the aid of the vertical electrical field, one particular particle under observation for hours at a time and to measure as many displacements as desired on it alone instead of assuming the identity of a great number of particles, as had been done in the case of suspensions in liquids and in De Broglie's experiments in gases.

2. Liquids are very much less suited than are gases to convincing tests of any kinetic hypothesis, for the reason that prior to Brownian-movement work we had no satisfactory kinetic theory of liquids at all.

3. The absolute amounts of the displacements of a given particle in air are 8 times greater and in hydrogen 15 times greater than in water.

4. By reducing the pressure to low values the displacements can easily be made from 50 to 200 times greater in gases than in liquids.

5. The measurements can be made independently of the most troublesome and uncertain factor involved in Brownian-movement work in liquids, namely, the factor  $K$ , which contains the radius of the particle and the law governing its motion through the liquid.

Accordingly, there was begun in the Ryerson Laboratory, in 1910, a series of very careful experiments in Brownian movements in gases. Svedberg,<sup>1</sup> in reviewing this subject in 1913, considers this "the only exact investigation of quantitative Brownian movements in gases." A brief summary of the method and results was published by the author.<sup>2</sup> A full account was

<sup>1</sup> *Jahrbuch der Radioaktivität und Elektronik*, X (1913), 513.

<sup>2</sup> *Science*, February 17, 1911.



published by Mr. Harvey Fletcher in May, 1911,<sup>1</sup> and further work on the variation of Brownian movements with pressure was presented by the author the year following.<sup>2</sup> The essential contribution of this work as regards method consisted in the two following particulars:

1. By combining the characteristic and fully tested equation of the oil-drop method, namely,

$$e = \frac{mg}{Fv_1}(v_1 + v_2)_0 = \frac{K}{F}(v_1 + v_2)_0 \dots \dots \dots (24)$$

with the Einstein Brownian-movement equation, namely,

$$\overline{\Delta x^2} = \frac{2RT}{NK} \tau \dots \dots \dots (25)$$

it was possible to obtain the product  $Ne$  without any reference to the size of the particle or the resistance of the medium to its motion. This quantity could then be compared with the same product obtained with great precision from electrolysis. The experimental procedure consists in balancing a given droplet and measuring, as in any Brownian-movement work, the quantity  $\overline{\Delta x^2}$ , then unbalancing it and measuring  $F$ ,  $v_1$  and  $(v_1 + v_2)_0$ ; the combination of (24) and (25) then gives

$$\overline{\Delta x^2} = \frac{2RT}{F} \frac{(v_1 + v_2)_0}{Ne} \tau \dots \dots \dots (26)$$

Since it is awkward to square each displacement  $\Delta x$  before averaging, it is preferable to modify by substituting from the Maxwell distribution law, which holds

<sup>1</sup> *Phys. Zeitschr.*, XII (1911), 202-8; see also *Phys. Rev.*, XXXIII (1911), 81.

<sup>2</sup> *Phys. Rev.*, I, N.S. (1913), 218.

for Brownian displacements as well as for molecular velocities, the relation

$$\overline{\Delta x} = \sqrt{\frac{2}{\pi} \overline{\Delta x^2}}.$$

We obtain thus

$$\overline{\Delta x} = \sqrt{\frac{4}{\pi} \frac{RT(v_1 + v_2)_0 \tau}{F(Ne)}} \dots \dots \dots (27)$$

or

$$Ne = \frac{4}{\pi} \frac{RT(v_1 + v_2)_0 \tau}{F(\overline{\Delta x})^2} \dots \dots \dots (28)$$

The possibility of thus eliminating the size of the particle, and with it the resistance of the medium to its motion can be seen at once from the simple consideration that *so long as we are dealing with one and the same particle* the ratio  $K$  between the force acting and the velocity produced by it must be the same, whether the acting force is due to gravity or an electrical field, as in the oil-drop experiments, or to molecular impacts as in Brownian-movement work. De Broglie might have made such an elimination and calculation of  $Ne$  in his work, had his Brownian displacements and mobilities in electric fields been made on one and the same particle, but when the two sets of measurements are made on different particles, such elimination would involve the very uncertain assumption of identity of the particles in both charge and size. Although De Broglie did actually make this assumption, he did not treat his data in the manner indicated, and the first publication of this method of measuring  $Ne$  as well as the first actual determination was made in the papers mentioned above.

Some time later E. Weiss reported similar work to the Vienna Academy.<sup>1</sup>

2. Although it is possible to make the test of *Ne* in just the method described and although it was so made in the case of one or two drops, Mr. Fletcher worked out a more convenient method, which involves expressing the displacements  $\Delta x$  in terms of the fluctuations in the time required by the particle to fall a given distance and thus dispenses with the necessity of balancing the drop at all. I shall present another derivation which is very simple and yet of unquestionable validity.

In equation (28) let  $\tau$  be the time required by the particle, if there were no Brownian movements, to fall between a series of equally spaced cross-hairs whose distance apart is  $d$ . In view of such movements the particle will have moved up or down a distance  $\Delta x$  in the time  $\tau$ . Let us suppose this distance to be up. Then the actual time of fall will be  $\tau + \Delta t$ , in which  $\Delta t$  is now the time it takes the particle to fall the distance  $\Delta x$ . If now  $\Delta t$  is small in comparison with  $\tau$ , that is, if  $\Delta x$  is small in comparison with  $d$  (say  $1/10$  or less), then we shall introduce a negligible error (of the order  $1/100$  at the most) if we assume that  $\Delta x = v_1 \Delta t$  in which  $v_1$  is the mean velocity under gravity. Replacing then in (28)  $(\overline{\Delta x})^2$  by  $v_1^2 (\overline{\Delta t})^2$ , in which  $(\overline{\Delta t})^2$  is the square of the average difference between an observed time of fall and the mean time of fall  $t_g$ , that is, the square of the average

<sup>1</sup> It was read before the Academy on July 6: *Wiener Berichte*, CXX (1911), II, 1021, but appeared first in print in the August 1st number of the *Phys. Zeitschr.* (1911), p. 63. Fletcher's article is found in brief in an earlier number of the same volume of the *Phys. Zeitschr.*, p. 203, and was printed in full in the July number of *Le Radium*, VIII (1911), 279.

fluctuation in the time of fall through the distance  $d$ , we obtain after replacing the ideal time  $\tau$  by the mean time  $t_g^r$

$$Ne = \frac{4RT(v_1 + v_2)_0 t_g}{\pi F v_1^2 (\overline{\Delta t})^2} \dots \dots \dots (29)$$

In any actual work  $\overline{\Delta t}$  will be kept considerably less than  $1/10$  the mean time  $t_g$  if the irregularities due to the observer's errors are not to mask the irregularities due to the Brownian movements, so that (29) is sufficient for practically all working conditions.<sup>1</sup>

The work of Mr. Fletcher and of the author was done by both of the methods represented in equations (28) and (29). The 9 drops reported upon in Mr. Fletcher's paper in 1911<sup>2</sup> yielded the results shown below in which  $n$  is the number of displacements used in each case in determining  $\overline{\Delta x}$  or  $\overline{\Delta'}$

TABLE XIII

$\sqrt{Ne} \times 10^7$	$n$
1.68	125
1.67	136
1.645	321
1.695	202
1.73	171
1.65	200
1.66	84
1.785	411
1.65	85

When weights are assigned proportional to the number of observations taken, as shown in the last column

<sup>1</sup> No error is introduced here if, as assumed,  $\overline{\Delta t}$  is small in comparison with  $t_g$ . However for more rigorous equations see Fletcher, *Phys. Rev.*, IV (1914), 442; also Smoluchowski, *Phys. Zeitschr.*, XVI (1915), 321.

<sup>2</sup> *Le Radium*, VIII (1911), 279; *Phys. Rev.*, XXXIII (1911), 107.

of Table XIII, there results for the weighted mean value which represents an average of 1,735 displacements,  $\sqrt{Ne} = 1.698 \times 10^7$  or  $Ne = 2.88 \times 10^{14}$  *electrostatic units*, as against  $2.896 \times 10^{14}$ , the value found in electrolysis. The agreement between theory and experiment is then in this case about as good as one-half of 1 per cent, which is well within the limits of observational error.

This work seemed to demonstrate, with considerably greater precision than had been attained in earlier Brownian-movement work and with a minimum of assumptions, the correctness of the Einstein equation, which is in essence merely the assumption that a particle in a gas, no matter how big or how little it is or out of what it is made, is moving about with a mean translatory kinetic energy which is a universal constant dependent only on temperature. To show how well this conclusion has been established I shall refer briefly to a few later researches.

In 1914 Dr. Fletcher, assuming the value of  $K$  which I had published<sup>1</sup> for oil drops moving through air, made new and improved Brownian-movement measurements in this medium and solved for  $N$  the original Einstein equation, which, when modified precisely as above by replacing  $\overline{\Delta x^2}$  by  $\frac{2}{\pi} (\overline{\Delta x})^2$  and  $(\overline{\Delta x})^2 = v_1^2 (\overline{\Delta t})^2$  becomes

$$N = \frac{4}{\pi} \frac{RT t_g}{K v_1^2 (\overline{\Delta t})^2} \dots\dots\dots (30)$$

He took, all told, as many as 18,837  $\Delta t$ 's, not less than 5,900 on a single drop, and obtained  $N = 60.3 \times 10^{22} \pm 1.2$ . This cannot be regarded as an altogether independent determination of  $N$ , since it involves my value

<sup>1</sup> *Phys. Rev.*, I (1913), 218.

of  $K$ . Agreeing, however, as well as it does with my value of  $N$ , it does show with much conclusiveness that both Einstein's equation and my corrected form of Stokes's equation apply accurately to the motion of oil drops of the size here used, namely, those of radius from  $2.79 \times 10^{-5}$  cm. to  $4.1 \times 10^{-5}$  cm. (280–400  $\mu\mu$ ).

In 1915 Mr. Carl Eyring tested by equation (29) the value of  $Ne$  on oil drops, of about the same size, in hydrogen and came out within .6 per cent of the value found in electrolysis, the probable error being, however, some 2 per cent.

Precisely similar tests on substances other than oils were made by Dr. E. Weiss<sup>1</sup> and Dr. Karl Przibram.<sup>2</sup> The former worked with silver particles only half as large as the oil particles mentioned above, namely, of radii between 1 and  $2.3 \times 10^{-5}$  cm. and obtained  $Ne = 10,700$  electromagnetic units instead of 9,650, as in electrolysis. This is indeed 11 per cent too high, but the limits of error in Weiss's experiments were in his judgment quite as large as this. K. Przibram worked on suspensions in air of five or six different substances, the radii varying from 200  $\mu\mu$  to 600  $\mu\mu$ , and though his results varied among themselves by as much as 100 per cent, his mean value came within 6 per cent of 9,650. Both of the last two observers took too few displacements on a given drop to obtain a reliable mean displacement, but they used so many drops that their mean  $Ne$  still has some significance.

It would seem, therefore, that the validity of Einstein's Brownian-movement equation had been pretty

<sup>1</sup> *Sitzungsber. d. k. Akad. d. Wiss. in Wien*, CXX (1911), II, 1021

<sup>2</sup> *Ibid.*, CXXI (1912), II, 950.



thoroughly established in gases. In liquids too it has recently been subjected to much more precise test than had formerly been attained. Nordlund,<sup>3</sup> in 1914, using minute mercury particles in water and assuming Stokes's Law of fall and Einstein's equations, obtained  $N = 59.1 \times 10^{22}$ . While in 1915 Westgren at Stockholm<sup>4</sup> by a very large number of measurements on colloidal gold, silver, and selenium particles, of diameter from  $65 \mu\mu$  to  $130 \mu\mu$  ( $6.5$  to  $13 \times 10^{-6}$  cm.), obtained a result which he thinks is correct to one-half of 1 per cent, this value is  $N = 60.5 \times 10^{22} \pm .3 \times 10^{22}$ , which agrees perfectly with the value which I obtained from the measurements on the isolation and measurement of the electron.

It has been because of such agreements as the foregoing that the last trace of opposition to the kinetic and atomic hypotheses of matter has disappeared from the scientific world, and that even Ostwald has been willing to make such a statement as 'that quoted on p. 10.

<sup>3</sup> *Ztschr. f. Phys. Chem.*, LXXXVII (1914), 40.

<sup>4</sup> *Die Brown'sche Bewegung besonders als Mittel zur Bestimmung der Avogadro'schen Konstante*, inaugural dissertation. Upsala: Almqvist & Wiksells Boktryckeri, 1915.

## CHAPTER VIII

### IS THE ELECTRON ITSELF DIVISIBLE?

It would not be in keeping with the method of modern science to make any dogmatic assertion as to the indivisibility of the electron. Such assertions used to be made in high-school classes with respect to the atoms of the elements, but the far-seeing among physicists, like Faraday, were always careful to disclaim any belief in the necessary ultimateness of the atoms of chemistry, and that simply because there existed until recently no basis for asserting anything about the insides of the atom. We knew that there was a smallest thing which took part in chemical reactions and we named that thing the atom, leaving its insides entirely to the future.

Precisely similarly the electron was defined as the smallest quantity of electricity which ever was found to appear in electrolysis, and nothing was then said or is now said about its necessary ultimateness. Our experiments have, however, now shown that this quantity is capable of isolation and exact measurement, and that all the kinds of charges which we have been able to investigate are exact multiples of it. Its value is  $4.774 \times 10^{-10}$  electrostatic units.

#### I. A SECOND METHOD OF OBTAINING $e$

I have presented one way of measuring this charge, but there is an indirect method of arriving at it which was worked out independently by Rutherford and Geiger<sup>1</sup>

<sup>1</sup> *Proc. Roy. Soc.*, A LXXXI (1908), 141, 161.

and Regener.<sup>1</sup> The unique feature in this method consists in actually counting the number of  $\alpha$ -particles shot off per second by a small speck of radium or polonium through a given solid angle and computing from this the number of these particles emitted per second by one gram of the radium or polonium. Regener made his determination by counting the scintillations produced on a diamond screen in the focal plane of his observing microscope. He then caught in a condenser all the  $\alpha$ -particles emitted per second by a known quantity of his polonium and determined the total quantity of electricity delivered to the condenser by them. This quantity of electricity divided by the number of particles emitted per second gave the charge on each particle. Because the  $\alpha$ -particles had been definitely proved to be helium atoms<sup>2</sup> and the value of  $\frac{e}{m}$  found for them showed that if they were helium they ought to carry double the electronic charge, Regener divided his result by 2 and obtained

$$e = 4.79 \times 10^{-10}.$$

He estimated his error at 3 per cent. Rutherford and Geiger made their count by letting the  $\alpha$ -particles from a speck of radium C shoot into a chamber and produce therein sufficient ionization by collision to cause an electrometer needle to jump every time one of them entered. These authors measured the total charge as Regener did and, dividing by 2 the charge on each  $\alpha$ -particle, they obtained

$$e = 4.65 \times 10^{-10}.$$

<sup>1</sup> *Sitzungsber. d. k. Preuss. Akad.*, XXXVIII (1909), 948.

<sup>2</sup> Rutherford and Royds, *Phil. Mag.*, XVII (1909), 281.

All determinations of  $e$  from radioactive data involve one or the other of these two counts, namely, that of Rutherford and Geiger or that of Regener. Thus, Boltwood and Rutherford<sup>1</sup> measured the total weight of helium produced in a second by a known weight of radium. Dividing this by the number of  $\alpha$ -particles (helium atoms) obtained from Rutherford and Geiger's count, they obtain the mass of one atom of helium from which the number in a given weight, or volume since the gas density is known, is at once obtained. They published for the number  $n$  of molecules in a gas per cubic centimeter at  $0^{\circ}.76$  cm.,  $n = 2.69 \times 10^{19}$ , which corresponds to

$$e = 4.81 \times 10^{-10}.$$

This last method, like that of the Brownian movements, is actually a determination of  $N$ , rather than of  $e$ , since  $e$  is obtained from it only through the relation  $Ne = 9,649.4$  electromagnetic units. Indeed, this is true of all methods of estimating  $e$ , so far as I am aware, except the oil-drop method and the Rutherford-Geiger-Regener method, and of these two the latter represents the measurement of the *mean* charge on an immense number of  $\alpha$ -particles.

Thus a person who wished to contend that the unit charge appearing in electrolysis is only a mean charge which may be made up of individual charges which vary widely among themselves, in much the same way in which the atomic weight assigned to *neon* has recently been shown to be a mean of the weights of at least two different elements inseparable chemically, could not be gainsaid, save on the basis of the evidence contained in

<sup>1</sup> *Phil. Mag.* (6), XXII (1911), 599.

the oil-drop experiments; for these constitute the only method which has been found of measuring directly the charge on each individual ion. It is of interest and significance for the present discussion, however, that the mean charge on an  $\alpha$ -particle has been directly measured and that it comes out, within the limits of error of the measurement, at exactly two electrons—as it should according to the evidence furnished by  $\frac{e}{m}$  measurements on the  $\alpha$ -particles.

## II. THE EVIDENCE FOR THE EXISTENCE OF A SUB-ELECTRON

Now, the foregoing contention has actually been made, and evidence has been presented which purports to show that electric charges exist which are much smaller than the electron. Since this raises what may properly be called the most fundamental question of modern physics, the evidence needs very careful consideration. This evidence can best be appreciated through a brief historical review of its origin.

The first measurements on the mobilities in electric fields of swarms of charged particles of microscopically visible sizes were made by H. A. Wilson<sup>1</sup> in 1903, as detailed in chap. iii. These measurements were repeated with modifications by other observers, including ourselves, during the years immediately following. De Broglie's modification, published in 1908,<sup>2</sup> consisted in sucking the metallic clouds discovered by Hemsalech and De Watteville,<sup>3</sup> produced by sparks or arcs between

<sup>1</sup> *Phil. Mag.* (6), V (1903), 429.

<sup>2</sup> *Comptes rendus*, CXLVI (1908), 624, 1010.

<sup>3</sup> *Ibid.*, CXLIV (1907), 1338.

metal electrodes, into the focal plane of an ultra-microscope and observing the motions of the individual particles in this cloud *in a horizontal electrical field produced by applying a potential difference to two vertical parallel plates* in front of the objective of his microscope. In this paper De Broglie first commented upon the fact that some of these particles were charged positively, some negatively, and some not at all, and upon the further fact that holding radium near the chamber caused changes in the charges of the particles. He promised quantitative measurements of the charges themselves. One year later he fulfilled the promise,<sup>1</sup> and at practically the same time Dr. Ehrenhaft<sup>2</sup> published similar measurements made with precisely the arrangement described by De Broglie a year before. Both men, as Dr. Ehrenhaft clearly pointed out,<sup>3</sup> while *observing* individual particles, obtained only a mean charge, since the different measurements entering into the evaluation of  $e$  were made on different particles. So far as concerns  $e$ , these measurements, as everyone agrees, were essentially cloud measurements like Wilson's.

In the spring and summer of 1909 I isolated individual water droplets and determined the charges carried by each one,<sup>4</sup> and in April, 1910, I read before the American Physical Society the full report on the oil-drop work in which the multiple relations between charges were established, Stokes's Law corrected, and  $e$  accurately

<sup>1</sup> *Ibid.*, CXLVIII (1909), 1316.

<sup>2</sup> *Phys. Zeitschr.*, X (1909), 308.

<sup>3</sup> *Ibid.*, XI (1910), 619.

<sup>4</sup> This paper was published in abstract in *Phys. Rev.*, XXX (1909), 560, and *Phil. Mag.*, XIX (1910), 209.



determined.<sup>1</sup> In the following month (May, 1910) Dr. Ehrenhaft,<sup>2</sup> having seen that a vertical condenser arrangement made possible, as shown theoretically and experimentally in the 1909 papers mentioned above, the independent determination of the charge on each individual particle, read the first paper in which he had used this arrangement in place of the De Broglie arrangement which he had used theretofore. He reported results identical in all essential particulars with those which I had published on water drops the year before, save that where I obtained consistent and simple multiple relations between charges carried by different particles he found no such consistency in these relations. The absolute values of these charges obtained on the assumption of Stokes's Law fluctuated about values considerably lower than  $4.6 \times 10^{-10}$ . Instead, however, of throwing the burden upon Stokes's Law or upon wrong assumptions as to the density of his particles, he remarked in a footnote that Cunningham's theoretical correction to Stokes's Law,<sup>3</sup> which he (Ehrenhaft) had just seen, would make his values come still lower, and hence that no failure of Stokes's Law could be responsible for his low values. He considered his results therefore as opposed to the atomic theory of electricity altogether, and in any case as proving the existence of charges much smaller than that of the electron.<sup>4</sup>

<sup>1</sup> This paper was published in abstract in *Phys. Rev.*, XXXI (1910), 92; *Science*, XXXII (1910), 436; *Phys. Zeitschr.*, XI (1910), 1097.

<sup>2</sup> *Wien. Ber.*, CXIX (1910), II, 809. This publication was apparently not issued before December, 1910, for it is not noted in *Naturae Novitates* before this date.

<sup>3</sup> *Proc. Roy. Soc.*, LXXXIII (1910), 360.

<sup>4</sup> These results were presented and discussed at great length in the fall of 1910; see *Phys. Zeitschr.*, XI (1910), 619, 940.

The apparent contradiction between these results and mine was explained when Mr. Fletcher and myself showed<sup>1</sup> experimentally that Brownian movements produced just such apparent fluctuations as Ehrenhaft observed when the  $e$  is computed, as had been done in his work, from one single observation of a speed under gravity and a corresponding one in an electric field. We further showed that the fact that his values fluctuated about too low an average value meant simply that his particles of gold, silver, and mercury were less dense because of surface impurities, oxides or the like, than he had assumed. The correctness of this explanation would be well-nigh demonstrated if the values of  $Ne$  computed by equations (28) or (29) in chap. vii from a large number of observations on Brownian movements always came out as in electrolysis, for in these equations no assumption has to be made as to the density of the particles. As a matter of fact, all of the nine particles studied by us and computed by Mr. Fletcher<sup>2</sup> showed the correct value of  $Ne$ , while only six of them as computed by me fell on, or close to, the line which pictures the law of fall of an oil drop through air (Fig. 5, p. 106). This last fact was not published in 1911 because it took me until 1913 to determine with sufficient certainty a second approximation to the complete law of fall of a droplet through air; in other words, to extend curves of the sort given in Fig. 5 to as large values of  $\frac{l}{a}$  as correspond to particles small enough to show large Brownian movements. As soon as I had done this I computed all the nine drops which gave correct values of  $Ne$  and

<sup>1</sup> *Phys. Zeitschr.*, XII (1911), 161; *Phys. Rev.*, XXXII (1911), 394.

<sup>2</sup> *Le Radium*, VIII (1911), 279; *Phys. Rev.*, XXXIII (1911), 107.

found that two of them fell way below the line, one more fell somewhat below, while one fell considerably above it. This meant obviously that these four particles were not spheres of oil alone, two of them falling much too slowly to be so constituted and one considerably too rapidly. There was nothing at all surprising about this result, since I had explained fully in my first paper on oil drops<sup>1</sup> that until I had taken great precaution to obtain dust-free air "the values of  $e_1$  came out differently, even for drops showing the same velocity under gravity." In the Brownian-movement work no such precautions to obtain dust-free air had been taken because we wished to test the general validity of equations (28) and (29). That we actually used in this test two particles which had a mean density very much smaller than that of oil and one which was considerably too heavy, was fortunate since it indicated that our result was indeed independent of the material used.

It is worthy of remark that in general, even with oil drops, almost all of those behaving abnormally fall too slowly, that is, they fall below the line of Fig. 5 and only rarely does one fall above it. This is because the dust particles which one is likely to observe, that is, those which remain long in suspension in the air, are either in general lighter than oil or else expose more surface and hence act as though they were lighter. When one works with particles made of dense metals this behavior will be still more marked, since all surface impurities of whatever sort will diminish the density. The possibility, however, of freeing oil-drop experiments from all such sources of error is shown by the fact that although during

<sup>1</sup> *Phys. Rev.*, XXXIII (1911), 366, 367.

the year 1915-16 I studied altogether as many as three hundred drops, there was not one which did not fall within less than 1 per cent of the line of Fig. 5. It will be shown, too, in this chapter, that in spite of the failure of the Vienna experimenters, it is possible under suitable conditions to obtain mercury drops which behave, even as to law of fall, in practically all cases with perfect consistency and normality.

When E. Weiss in Prag and K. Przibram in the Vienna laboratory itself, as explained in chap. vii, had found that  $Ne$  for all the substances which they worked with, including silver particles like those used by Ehrenhaft, gave about the right value of  $Ne$ , although yielding much too low values of  $e$  when the latter was computed from the law of fall of *silver* particles, the scientific world practically universally accepted our explanation of Ehrenhaft's results and ceased to concern itself with the idea of a sub-electron.<sup>1</sup>

In 1914 and 1915, however, Professor Ehrenhaft<sup>2</sup> and two of his pupils, F. Zerner<sup>3</sup> and D. Konstantinowsky,<sup>4</sup> published new evidence for the existence of such a sub-electron and the first of these authors has kept up some discussion of the matter up to the present. These experimenters make three contentions. The first is essentially that they have now determined  $Ne$  for their particles by equation (29); and although in many instances it comes out as in electrolysis, in some instances it comes out from

<sup>1</sup> See R. Pohl, *Jahrbuch der Radioaktivität und Elektronik*, VII (1912), 431.

<sup>2</sup> *Wien. Sitzungsber.*, CXXIII (1914), 53-155; *Ann. d. Phys.*, XLIV (1914), 657.

<sup>3</sup> *Phys. Zeitschr.*, XVI (1915), 10.

<sup>4</sup> *Ann. d. Phys.*, XLVI (1915), 261.

20 per cent to 50 per cent too low, while in a few cases it is as low as one-fourth or one-fifth of the electrolytic value. Their procedure is in general to publish, not the value of  $Ne$ , but, instead, the value of  $e$  obtained from  $Ne$  by inserting Perrin's value of  $N$  ( $70 \times 10^{22}$ ) in (29) and then solving for  $e$ . This is their method of determining  $e$  "from the Brownian movements."

Their second contention is the same as that originally advanced, namely, that, in some instances, when  $e$  is determined with the aid of Stokes's Law of fall (equation 12, p. 91), even when Cunningham's correction or my own (equation 15, p. 101) is employed, the result comes out very much lower than  $4.77 \times 10^{-10}$ . Their third claim is that the value of  $e$ , determined as just explained from the Brownian movements, is in general higher than the value computed from the law of fall, and that the departures become greater and greater the smaller the particle. These observers conclude therefore that we oil-drop observers failed to detect sub-electrons because our droplets were too big to be able to reveal their existence. The minuter particles which they study, however, seem to them to bring these sub-electrons to light. *In other words, they think the value of the smallest charge which can be caught from the air actually is a function of the radius of the drop on which it is caught, being smaller for small drops than for large ones.*

Ehrenhaft and Zerner even analyze our report on oil droplets and find that these also show in certain instances indications of sub-electrons, for they yield in these observers' hands too low values of  $e$ , whether computed from the Brownian movements or from the law of fall.

When the computations are made in the latter way  $e$  is found, according to them, to decrease with decreasing radius, as is the case in their experiments on particles of mercury and gold.

### III. CAUSES OF THE DISCREPANCIES

Now, the single low value of  $Ne$  which these authors find in the oil-drop work is obtained by computing  $Ne$  from some twenty-five observations on the times of fall, and an equal number on the times of rise, of a particle which, before we had made any  $Ne$  computations at all, we reported upon<sup>1</sup> for the sake of showing that the Brownian movements would produce just such fluctuations as Ehrenhaft had observed when the conditions were those under which he worked. When I compute  $Ne$  by equation (29), using merely the twenty-five times of fall, I find the value of  $Ne$  comes out 26 per cent low, just as Zerner finds it to do. If, however, I omit the first reading it comes out but 11 per cent low. In other words, the omission of one single reading changes the result by 15 per cent. Furthermore, Fletcher<sup>2</sup> has shown that these same data, though treated entirely legitimately, but with a slightly different grouping than that used by Zerner, can be made to yield exactly the right value of  $Ne$ . This brings out clearly the futility of attempting to test a statistical theorem by so few observations as twenty-five, which is nevertheless more than Ehrenhaft usually uses on his drops. Furthermore, I shall presently show that unless one observes under carefully chosen conditions, his own errors of observation

<sup>1</sup> *Phys. Zeitschr.*, XII (1911), 162.

<sup>2</sup> *Ibid.*, XVI (1915), 316.



and the slow evaporation of the drop tend to make  $Ne$  obtained from equation (29) come out too low, and these errors may easily be enough to vitiate the result entirely. *There is, then, not the slightest indication in any work which we have thus far done on oil drops that  $Ne$  comes out too small.*

Next consider the apparent *variation in  $e$*  when it is computed from the law of fall. Zerner computes  $e$  from my law of fall in the case of the nine drops published by Fletcher, in which  $Ne$  came out as in electrolysis, and finds that one of them yields  $e=6.66\times 10^{-10}$ , one  $e=3.97\times 10^{-10}$ , one  $e=1.32\times 10^{-10}$ , one  $e=1.7\times 10^{-10}$ , while the other five yield about the right value, namely,  $4.8\times 10^{-10}$ . In other words (as stated on p. 165 above), five of these drops fall exactly on my curve (Fig. 5), one falls somewhat above it, one somewhat below, while two are entirely off and very much too low. These two, therefore, I concluded were not oil at all, but dust particles. Since Zerner computes the radius from the rate of fall, these two dust particles which fall much too slowly, and therefore yield too low values of  $e$ , must, of course, yield correspondingly low values of  $a$ . Since they are found to do so, Zerner concludes that our oil drops, as well as Ehrenhaft's mercury particles, yield decreasing values of  $e$  with decreasing radius. His own tabulation does not show this. It merely shows three erratic values of  $e$ , two of which are very low and one rather high. But a glance at all the other data which I have published on oil drops shows the complete falsity of this position,<sup>1</sup> *for these data show that after I had eliminated dust all of my particles yielded exactly the same value of "e" whatever their*

<sup>1</sup> *Phys. Rev.*, II (1913), 138.

size<sup>1</sup>. The only possible interpretation then which could be put on these two particles which yielded correct values of  $Ne$ , but too slow rates of fall, was that which I put upon them, namely, that they were not spheres of oil.

As to the Vienna data on mercury and gold, Dr. Ehrenhaft publishes, all told, data on just sixteen particles and takes for his Brownian-movement calculations on the average *fifteen times of fall and fifteen of rise on each, the smallest number being 6 and the largest 27*. He then computes his statistical average  $(\overline{\Delta t})^2$  from observations of this sort. Next he assumes Perrin's value of  $N$ , namely,  $70 \times 10^{22}$ , which corresponds to  $e = 4.1$ , and obtains instead by the Brownian-movement method, i.e., the  $Ne$  method, the following values of  $e$ , the exponential term being omitted for the sake of brevity: 1.43, 2.13, 1.38, 3.04, 3.5, 6.92, 4.42, 3.28, .84. Barring the first three and the last of these, the mean value of  $e$  is just about what it should be, namely, 4.22 instead of 4.1. Further, the first three particles are the heaviest ones, the first one falling between his cross-hairs in 3.6 seconds, and its fluctuations in time of fall are from 3.2 to 3.85 seconds, that is, three-tenths of a second on either side of the mean value. *Now, these fluctuations are only slightly greater than those which the average observer will make in timing the passage of a uniformly moving body across equally spaced cross-hairs*. This means that in these observations two nearly equally potent causes were operating to produce fluctuations. The observed  $\Delta t$ 's were, of course, then, larger than those due to Brownian movements alone, and might easily, with but a few observations, be two or three times as large. Since

<sup>1</sup> See *Phys. Rev.*, II (1913), 134-35.

$(\overline{\Delta t})^2$  appears in the denominator of equation (29), it will be seen at once that because of the observer's timing errors a series of observed  $\Delta t$ 's will always tend to be larger than the  $\Delta t$  due to Brownian movements alone, and hence that the Brownian-movement method always tends to yield too low a value of  $Ne$ , and accordingly too low a value of  $e$ . *It is only when the observer's mean error is wholly negligible in comparison with the Brownian-movement fluctuations that this method will not yield too low a value of  $e$ .* The overlooking of this fact is, in my judgment, one of the causes of the low values of  $e$  recorded by Dr. Ehrenhaft.

Again, in the original work on mercury droplets which I produced both by atomizing liquid mercury and by condensing the vapor from boiling mercury,<sup>1</sup> I noticed that such droplets evaporated for a time even more rapidly than oil, and other observers who have since worked with mercury have reported the same behavior.<sup>2</sup> The amount of this effect may be judged from the fact that one particular droplet of mercury recently under observation in this laboratory had at first a speed of 1 cm. in 20 seconds, which changed in half an hour to 1 cm. in 56 seconds. The slow cessation, however, of this evaporation indicates that the drop slowly becomes coated with some sort of protecting film. Now, if any evaporation whatever is going on while successive times of fall are being observed—and as a matter of fact changes due to evaporation or condensation are always taking place to some extent—the apparent  $(\overline{\Delta t})^2$  will be larger than that due to Brownian movements, even

<sup>1</sup> *Phys. Rev.*, XXXII (1911), 389.

<sup>2</sup> See Schidlof et Karpowicz, *Comptes rendus*, CLVIII (1914), 1912.

though these movements are large enough to prevent the observer from noticing, in taking twenty or thirty readings, that the drop is continually changing. These changes combined with the fluctuations in  $t$  due to the observer's error are sufficient, I think, to explain all of the low values of  $e$  obtained by Dr. Ehrenhaft by the Brownian-movement method. Indeed, I have myself repeatedly found  $Ne$  coming out less than half of its proper value *until I corrected for the evaporation of the drop*, and this was true when the evaporation was so slow that its rate of fall changed but 1 or 2 per cent in a half-hour. But it is not merely evaporation which introduces an error of this sort. The running down of the batteries, the drifting of the drop out of focus, or anything which causes changes in the times of passage across the equally spaced cross-hairs tends to decrease the apparent value of  $Ne$ . *There is, then, so far as I can see, no evidence at all in any of the data published to date that the Brownian-movement method actually does yield too low a value of "e," and very much positive evidence that it does not was given in the preceding chapter.*

Indeed, the same type of Brownian-movement work which Fletcher and I did upon oil-drops ten years ago (see preceding chapter) has recently been done in Vienna with the use of particles of selenium, and with results which are in complete harmony with our own. The observer, E. Schmid,<sup>1</sup> takes as many as 1,500 "times of fall" upon a given particle, the radius of which is in one case as low as  $5 \times 10^{-6}$  cm.—quite as minute as any used by Dr. Ehrenhaft—and obtains in all cases values of  $e$

<sup>1</sup> E. Schmid, *Wien. Akad. Ber.*, CXXIX (1920), 813, and *ZfP*, V (1921), 27.

by "the Brownian-movement method" which are in as good agreement with our own as could be expected in view of the necessary observational error. This complete check of our work in Vienna itself should close the argument so far as the Brownian movements are concerned.

That  $e$  and  $a$  computed from the law of fall become farther and farther removed from the values of  $e$  and  $a$  computed from the Brownian movements, the smaller these particles appear to be, is just what would be expected if the particles under consideration have surface impurities or non-spherical shapes or else are not mercury at all.<sup>1</sup> If, further, *exact multiple relations hold for them*, as at least a dozen of us, including Dr. Ehrenhaft himself, now find that they invariably do, there is scarcely any other interpretation possible except that of incorrect assumptions as to density.<sup>1</sup> Again, the fact that these data are all taken when the observers are working with the exceedingly dense substances, mercury and gold, *volatilized in an electric arc*, and when, therefore, anything not mercury or gold, but assumed to be, would yield very low values of  $e$  and  $a$ , is in itself a very significant circumstance. The further fact that Dr. Ehrenhaft implies that normal values of  $e$  very frequently appear in his work,<sup>2</sup> while these low erratic drops represent only a part of the data taken, is suggestive. When

<sup>1</sup> R. Bär, in a series of articles recently summarized in *Die Naturwissenschaften*, Vols. XIV and XV, 1922, has emphasized this point. His data serve merely as a new check upon the work found in our preceding tables.

<sup>2</sup> "Die bei grösseren Partikeln unter gewissen Umständen bei gleicher Art der Erzeugung häufig wiederkehrenden höheren Quanten waren dann etwa als stabilere räumliche Gleichgewichtsverteilungen



one considers, too, that in place of the beautiful consistency and duplicability shown in the oil-drop work, Dr. Ehrenhaft and his pupils never publish data on any two particles which yield the same value of  $e$ , but instead find only irregularities and erratic behavior,<sup>1</sup> just as they would expect to do with non-uniform particles, or with particles having dust specks attached to them, one wonders why any explanation other than the foreign-material one, which explains all the difficulties, has ever been thought of. As a matter of fact, in our work with mercury droplets, we have found that the initial rapid evaporation gradually ceases, just as though the droplets had become coated with some foreign film which prevents further loss. Dr. Ehrenhaft himself, in speaking of the Brownian movements of his metal particles, comments on the fact that they seem at first to show large movements which grow smaller with time.<sup>2</sup> This is just what would happen if the radius were increased by the growth of a foreign film.

Now what does Dr. Ehrenhaft say to these very obvious suggestions as to the cause of his troubles? Merely that he has avoided all oxygen, and hence that

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dieser Sub-electron anzusehen, die sich unter gewissen Umständen ergeben."—*Wien. Ber.*, CXXIII, 59.

<sup>1</sup> Their whole case is summarized in the tables in *Ann. d. Phys.*, XLIV (1914), 693, and XLVI (1915), 292, and it is recommended that all interested in this discussion take the time to glance at the data on these pages, for the data themselves are so erratic as to render discussion needless.

<sup>2</sup> "Wie ich in meinen früheren Publikationen erwähnt habe, zeigen die ultramikroskopischen Metallpartikel, unmittelbar nach der Erzeugung beobachtet, eine viel lebhaftere Brownsche Bewegung als nach einer halben Stunde."—*Phys. Zeitschr.*, XII, 98.



an oxide film is impossible. *Yet he makes his metal particle by striking an electric arc between metal electrodes.* This, as everyone knows, brings out all sorts of occluded gases. Besides, chemical activity in the electric arc is tremendously intense, so that there is opportunity for the formation of all sorts of higher nitrides, the existence of which in the gases coming from electric arcs has many times actually been proved. Dr. Ehrenhaft says further that he photographs big mercury droplets and finds them spherical and free from oxides. But the fact that some drops are pure mercury is no reason for assuming that all of them are, and it is only the data on those which are not which he publishes. Further, because big drops which he can see and measure are of mercury is no justification at all for assuming that sub-microscopic particles are necessarily also spheres of pure mercury. In a word, Dr. Ehrenhaft's tests as to sphericity and purity are all absolutely worthless as applied to the particles in question, which according to him have radii of the order  $10^{-6}$  cm.—a figure a hundred times below the limit of sharp resolution.

#### IV. THE BEARING OF THE VIENNA WORK ON THE QUESTION OF THE EXISTENCE OF A SUB-ELECTRON

But let us suppose that these observers do actually work with particles of pure mercury and gold, as they think they do, and that the observational and evaporational errors do not account for the low values of  $N_e$ . Then what conclusion could legitimately be drawn from their data? Merely this and nothing more, that (1) Einstein's Brownian-movement equation is not universally applicable, and (2) that the law of motion of

their very minute charged particles through air is not yet fully known.<sup>1</sup> So long as they find exact multiple relationships, as Dr. Ehrenhaft now does, between the charges carried by a given particle when its charge is changed by the capture of ions or the direct loss of electrons, the charges on these ions must be the same as the ionic charges which I have accurately and consistently measured and found equal to  $4.77 \times 10^{-10}$  electrostatic units; for they, in their experiments, capture exactly the same sort of ions, produced in exactly the same way as those which I captured and measured in my experiments. That these same ions have one sort of a charge when captured by a big drop and another sort when captured by a little drop is obviously absurd. *If they are not the same ions which are caught, then in order to reconcile the results with the existence of the exact multiple relationship found by Dr. Ehrenhaft as well as ourselves, it would be necessary to assume that there exist in the air an infinite number of different kinds of ionic charges corresponding to the infinite number of possible radii of drops, and that when a powerful electric field drives all of these ions toward a given drop this drop selects in each instance just the charge which corresponds to its particular radius.* Such an assumption is not only too grotesque for serious consideration, but it is directly contradicted by my experiments, for I have repeatedly pointed out that with a given value of  $\frac{l}{a}$  I obtain exactly the same value of  $e_1$ , whether I work with big drops or with little ones.

<sup>1</sup> In my own opinion this is a conclusion contrary to fact, since in a recent paper (see *Phys. Rev.*, July, 1923) I have fully established the "Complete Law of Fall."

V. NEW PROOF OF THE CONSTANCY OF  $e$ 

For the sake of subjecting the constancy of  $e$  to the most searching test, I have made new measurements of the same kind as those heretofore reported, but using now a range of sizes which overlaps that in which Dr. Ehrenhaft works. I have also varied through wide limits the nature and density of both the gas and the drops. Fig. 13 (I) contains new oil-drop data taken in air; Fig. 13 (II) similar data taken in hydrogen. The radii of these drops, computed by the very exact method given in the *Physical Review*,<sup>1</sup> vary tenfold, namely, from .000025 cm. to .00023 cm. Dr. Ehrenhaft's range is from .000008 cm. to .000025 cm. It will be seen that these drops fall in every instance on the lines of Fig. 13, I and II, and hence that they all yield exactly the same value of  $e^{\frac{1}{2}}$ , namely,  $61.1 \times 10^{-8}$ . The details of the measurements, which are just like those previously given, will be entirely omitted. There is here *not a trace of an indication that the value of "e" becomes smaller as "a" decreases*. The points on these two curves represent consecutive series of observations, not a single drop being omitted in the case of either the air or the hydrogen. This shows the complete uniformity and consistency which we have succeeded in obtaining in the work with oil drops.

That mercury drops show a similar behavior was somewhat imperfectly shown in the original observations which I published on mercury.<sup>2</sup> I have since fully confirmed the conclusions there reached. That mercury drops can with suitable precautions be made to behave

<sup>1</sup> II (1913), 117.

<sup>2</sup> *Ibid.*, CCC (1911), 389-90.

practically as consistently as oil is shown in Fig. 13 (III), which represents data obtained by blowing into the observing chamber above the pinhole in the upper plate a cloud of mercury droplets formed by the condensation of the vapor arising from boiling mercury. These results have been obtained in the Ryerson Laboratory with my apparatus by Mr. John B. Derieux. Since the pressure was here always atmospheric, the drops progress in the order of size from left to right, the largest having a diameter about three times that of the smallest, the radius of which is .00003244 cm. The original data may be found in the *Physical Review*, December, 1916. In Fig. 13 (IV) is found precisely similar data taken with my apparatus by Dr. J. Y. Lee on solid spheres of shellac falling in air.<sup>1</sup> Further, very beautiful work, of this same sort, also done with my apparatus, has recently been published by Dr. Yoshio Ishida (*Phys. Rev.*, May, 1923), who, using many different gases, obtains a group of lines like those shown in Fig. 13, *all of which though of different slopes, converge upon one and the same value of " $e^2$ ," namely,  $61.08 \times 10^{-8}$ .*

*These results establish with absolute conclusiveness the correctness of the assertion that the apparent value of the electron is not in general a function of the gas in which the particle falls, of the materials used, or of the radius of the drop on which it is caught, even when that drop is of mercury, and even when it is as small as some of those*

<sup>1</sup> The results shown in Fig. 13 do not lay claim to the precision reached in those recorded in Table X and Fig. 10. No elaborate precautions were here taken in the calibration of the Hipp chronoscope and the voltmeter, and it is due to slight errors discovered later in these calibrations that the slope of line I in Fig. 13 is not quite in agreement with the slope in Fig. 10



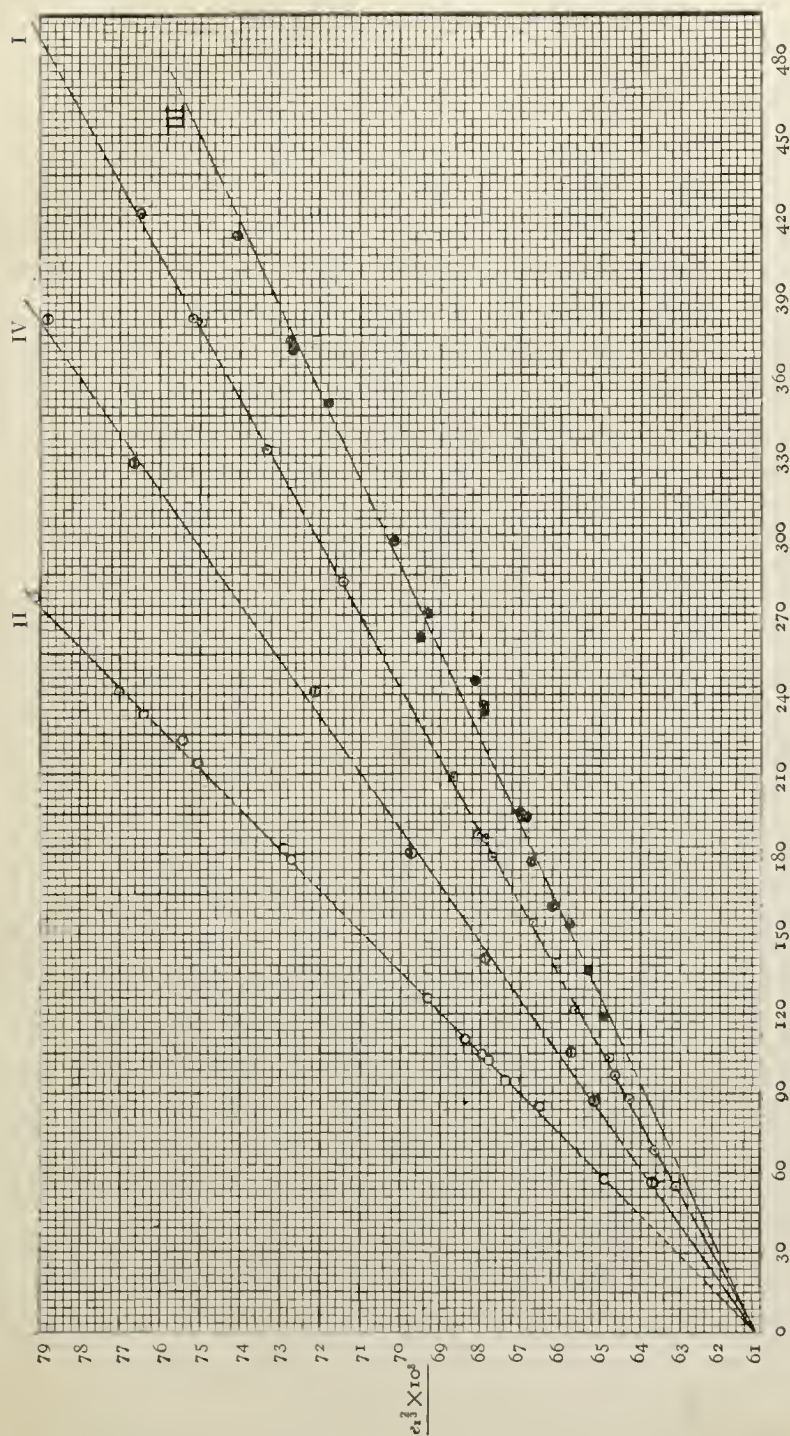


FIG. 13

with which Dr. Ehrenhaft obtained his erratic results. If it appears to be so with his drops, the cause cannot possibly be found in actual fluctuations in the charge of the electron without denying completely the validity of my results. But these results have now been checked, in their essential aspects, by scores of observers, including Dr. Ehrenhaft himself. Furthermore, it is not my results alone with which Dr. Ehrenhaft's contention clashes. The latter is at variance also with all experiments like those of Rutherford and Geiger and Regener on the measurement of the charges carried by  $\alpha$ - and  $\beta$ -particles, for these are infinitely smaller than any particles used by Dr. Ehrenhaft; and if, as he contends, the value of the unit out of which a charge is built up is smaller and smaller the smaller the capacity of the body on which it is found, then these  $\alpha$ -particle charges ought to be extraordinarily minute in comparison with the charges on our oil drops. Instead of this, the charge on the  $\alpha$ -particle comes out exactly twice the charge which I measure in my oil-drop experiments.

While then it would not be in keeping with the spirit or with the method of modern science to make any dogmatic assertion about the existence or non-existence of a sub-electron, it can be asserted with entire confidence that there has not appeared up to the present a scrap of evidence for the existence of charges smaller than the electron. If all of Dr. Ehrenhaft's assumptions as to the nature of his particles were correct, then his experiments would mean simply that Einstein's Brownian-movement equation is not of universal validity and that the law of motion of minute charged particles is quite different from that which he has assumed. It is exceedingly unlikely that



either of these results can be drawn from his experiments, for Nordlund<sup>1</sup> and Westgren<sup>2</sup> have apparently verified the Einstein equation in liquids with very much smaller particles than Dr. Ehrenhaft uses; and, on the other hand, while I have worked with particles as small as  $2 \times 10^{-5}$  cm. and with values of  $\frac{l}{a}$  as large as 135, which is very much larger than any which appear in the work of Dr. Ehrenhaft and his pupils, I have thus far found no evidence of a law of motion essentially different from that which I published in 1913, and further elaborated and refined in 1923.

*There has then appeared up to the present time no evidence whatever for the existence of a sub-electron.* The chapter having to do with its discussion is now considered for the present at least to have been closed,<sup>3</sup> but it constitutes an interesting historical document worthy of study as an illustration on the one hand of the solidity of the foundations upon which the atomic theory of electricity now rests, and on the other hand of the severity of the gauntlet of criticism which new results must run before they gain admission to the body of established truth in physics.

<sup>1</sup> *Zeit. für Phys. Chem.*, LXXXVII (1914), 40.

<sup>2</sup> Inaugural Dissertation von Arne Westgren, *Untersuchungen über Brownsche Bewegung*, Stockholm, 1915.

<sup>3</sup> R. Bär, "Der Streit um das Elektron," *Die Naturwissenschaften*, 1922.

## CHAPTER IX

### THE STRUCTURE OF THE ATOM

We have shown in the preceding chapters how within the last two decades there has been discovered beneath the nineteenth-century world of molecules and atoms a wholly new world of electrons, the very existence of which was undreamed of twenty years ago. We have seen that these electrons, since they can be detached by X-rays from all kinds of neutral atoms, must be constituents of all atoms. Whether or not they are the sole constituents we have thus far made no attempt to determine. We have concerned ourselves with studying the properties of these electrons themselves and have found that they are of two kinds, negative and positive, which are, however, exactly alike in strength of charge but wholly different in inertia or mass, the negative being commonly associated with a mass which is but  $1/1,845$  of that of the lightest known atom, that of hydrogen, while the positive appears never to be associated with a mass smaller than that of the hydrogen atom. We have found how to isolate and measure accurately the electronic charge and have found that this was the key which unlocked the door to many another otherwise inaccessible physical magnitude. It is the purpose of this chapter to consider certain other fields of exact knowledge which have been opened up through the measurement of the electron, and in particular to discuss what the physicist, as he has peered with his newly discovered agencies, X-rays, radioactivity, ultra-violet

light, etc., into the insides of atoms, has been able to discover regarding the numbers and sizes and relative positions and motions of these electronic constituents, and to show how far he has gone in answering the question as to whether the electrons are the sole building-stones of the atoms.

## I. THE SIZES OF ATOMS

One of the results of the measurement of the electronic charge was to make it possible to find the quantity which is called the diameter of an atom with a definiteness and precision theretofore altogether unattained.

It was shown in chap. v that the determination of  $e$  gave us at once a knowledge of the exact number of molecules in a cubic centimeter of a gas. Before this was known we had fairly satisfactory information as to the relative diameters of different molecules, for we have known for a hundred years that different gases when at the same temperature and pressure possess the same number of molecules per cubic centimeter (Avogadro's rule). From this it is at once evident that, as the molecules of gases eternally dart hither and thither and ricochet against one another and the walls of the containing vessel, the average distance through which one of them will go between collisions with its neighbors will depend upon how big it is. The larger the diameter the less will be the mean distance between collisions—a quantity which is technically called “the mean free path.” Indeed, it is not difficult to see that in different gases the mean free path  $l$  is an inverse measure of the molecular cross-section. The exact relation is easily deduced (see Appendix E). It is

$$l = \frac{1}{\pi n d^2 \sqrt{2}} \dots \dots \dots (31)$$

in which  $d$  is the molecular diameter and  $n$  is the number of molecules per cubic centimeter of the gas. Now, we have long had methods of measuring  $l$ , for it is upon this that the coefficient of viscosity of the gas largely depends. When, therefore, we have measured the viscosities of different gases we can compute the corresponding  $l$ 's, and then from equation (31) the relative diameters  $d$ , since  $n$  is the same for all gases at the same temperature and pressure. But the absolute value of  $d$  can be found only after the absolute value of  $n$  is known. If we insert in equation (31) the value of  $n$  found from  $e$  by the method presented in chap. v, it is found that the average diameter of the atom of the monatomic gas helium is  $2 \times 10^{-8}$  cm., that of the diatomic hydrogen molecule is a trifle more, while the diameters of the molecules of the diatomic gases, oxygen and nitrogen, are 50 per cent larger.<sup>1</sup> This would make the diameter of a single atom of hydrogen a trifle smaller, and that of a single atom of oxygen or nitrogen a trifle larger than that of helium. By the average molecular diameter we mean the average distance to which the centers of two molecules approach one another in such impacts as are continually occurring in connection with the motions of thermal agitation of gas molecules—this and nothing more.

As will presently appear, the reason that two molecules thus rebound from one another when in their motion of thermal agitation their centers of gravity approach to a distance of about  $2 \times 10^{-8}$  cm. is presumably that the atom is a system with negative electrons in its outer regions. When these negative electrons in two

<sup>1</sup> R. A. Millikan, *Phys. Rev.*, XXXII (1911), 397.

different systems which are coming into collision approach to about this distance, the repulsions between these similarly charged bodies begin to be felt, although at a distance the atoms are forceless. With decreasing distance this repulsion increases very rapidly until it becomes so great as to overcome the inertias of the systems and drive them asunder.

## II. THE RADIUS OF THE ELECTRON FROM THE ELECTROMAGNETIC THEORY OF THE ORIGIN OF MASS

The first estimates of the volume occupied by a single one of the electronic constituents of an atom were obtained from the electromagnetic theory of the origin of mass, and were therefore to a pretty large degree speculative, but since these estimates are strikingly in accord with results which follow from direct experiments and are independent of any theory, and since, further, they are of extraordinary philosophic as well as historic interest, they will briefly be presented here.

Since Rowland proved that an electrically charged body in motion is an electrical current the magnitude of which is proportional to the speed of motion of the charge, and since an electric current, by virtue of the property called its self-induction, opposes any attempt to increase or diminish its magnitude, it is clear that an electrical charge, as such, possesses the property of inertia. But inertia is the only invariable property of matter. It is the quantitative measure of matter, and matter quantitatively considered is called *mass*. It is clear, then, theoretically, that an electrically charged pith ball must possess more mass than the same pith ball when uncharged. But when we compute how much

the mass of a pith ball is increased by any charge which we can actually get it to hold, we find that the increase is so extraordinarily minute as to be hopelessly beyond the possibility of experimental detection. However, the method of making this computation, which was first pointed out by Sir J. J. Thomson in 1881,<sup>1</sup> is of unquestioned validity, so that we may feel quite sure of the correctness of the result. Further, when we combine the discovery that an electric charge possesses the distinguishing property of matter, namely, inertia, with the discovery that all electric charges are built up out of electrical specks all alike in charge, we have made it entirely legitimate to consider an electric current as *the passage of a definite, material, granular substance along the conductor. In other words, the two entities, electricity and matter, which the nineteenth century tried to keep distinct, begin to look like different aspects of one and the same thing.*

But, though we have thus justified the statement that electricity is material, have we any evidence as yet that all matter is electrical—that is, that all inertia is of the same origin as that of an electrical charge? The answer is that we have *evidence*, but as yet no *proof*. The theory that this is the case is still a speculation, but one which rests upon certain very significant facts. These facts are as follows:

If a pith ball is spherical and of radius  $a$ , then the mass  $m$  due to a charge  $E$  spread uniformly over its surface is given, as is shown in Appendix D by,

$$m = \frac{2}{3} \frac{E^2}{a} \dots\dots\dots (32)$$

<sup>1</sup> J. J. Thomson, *Phil. Mag.*, XI (1881), 229.



The point of especial interest in this result is that the mass is inversely proportional to the radius, so that the smaller the sphere upon which we can condense a given charge  $E$  the larger the mass of that charge. If, then, we had any means of measuring the minute increase in mass of a pith ball when we charge it electrically with a known quantity of electricity  $E$ , we could compute from equation (32) the size of this pith ball, even if we could not see it or measure it in any other way. This is much the sort of a position in which we find ourselves with respect to the negative electron. We can measure its mass, and it is found to be accurately  $1/1,845$  of that of the hydrogen atom. We have measured accurately its charge and hence can compute the radius  $a$  of *the equivalent sphere*, that is, the sphere over which  $e$  would have to be uniformly distributed to have the observed mass, provided we assume that the observed mass of the electron is all due to its charge.

The justification for such an assumption is of two kinds. First, since we have found that electrons are constituents of all atoms and that mass is a property of an electrical charge, it is of course in the interests of simplicity to assume that all the mass of an atom is due to its contained electrical charges, rather than that there are two wholly different kinds of mass, one of electrical origin and the other of some other sort of an origin. Secondly, if the mass of a negative electron is all of electrical origin, then we can show from electromagnetic theory that this mass ought to be independent of the speed with which the electron may chance to be moving unless that speed approaches close to the speed of light. But from one-tenth the speed of light up to

that speed the mass ought to vary with speed in a definitely predictable way.

Now, it is a piece of rare good fortune for the testing of this theory that radium actually does eject negative electrons with speeds which can be accurately measured and which do vary from three-tenths up to ninety-eight hundredths of that of light. *It is further one of the capital discoveries of the twentieth century<sup>1</sup> that within these limits the observed rate of variation of the mass of the negative electron with speed agrees accurately with the rate of variation computed on the assumption that this mass is all of electrical origin.* Such is the experimental argument for the electrical origin of mass.<sup>2</sup>

Solving then equation (32) for  $a$ , we find that the radius of the sphere over which the charge  $e$  of the negative electron would have to be distributed to have the observed mass is but  $2 \times 10^{-13}$  cm., or but one fifty-thousandth of the radius of the atom ( $10^{-8}$  cm.). From this point of view, then, the negative electron represents a charge of electricity which is condensed into an exceedingly minute volume. In fact, its radius cannot be larger in comparison with the radius of the atom than is the radius of the earth in comparison with the radius of her orbit about the sun.

In the case of the positive electron there is no direct experimental justification for the assumption that the mass is also wholly of electrical origin, for we cannot impart to the positive electrons speeds which approach the speed of light, nor have we as yet found in nature

<sup>1</sup> Bucherer, *Annalen der Physik*, XXVIII (1900), 513.

<sup>2</sup> The inadequacy in this argument arises from the fact that Einstein's Theory of Relativity requires that all mass, whether of electromagnetic origin or not, varies in just this way with speed.

any of them which are endowed with speeds greater than about one-tenth that of light. But in view of the experimental results obtained with the negative electron, the carrying over of the same assumption to the positive electron is at least natural. Further, if this step be taken, it is clear from equation (32), since  $m$  for the positive is nearly two thousand times larger than  $m$  for the negative, that  $a$  for the positive can be only  $1/2,000$  of what it is for the negative. In other words, the size of the positive electron would be to the size of the negative as a sphere having a two-mile radius would be to the size of the earth. From the standpoint, then, of the electromagnetic theory of the origin of mass, the dimensions of the negative and positive constituents of atoms in comparison with the dimensions of the atoms themselves are like the dimensions of the planets and asteroids in comparison with the size of the solar system. All of these computations, whatever their value, are rendered possible by the fact that  $e$  is now known.

Now we know from methods which have nothing to do with the electromagnetic theory of the origin of mass, that the excessive minuteness predicted by that theory for both the positive and the negative constituents of atoms is in fact correct, though we have no evidence as to whether the foregoing ratio is right.

### III. DIRECT EXPERIMENTAL PROOF OF THE EXCESSIVE MINUTENESS OF THE ELECTRONIC CONSTITUENTS OF ATOMS

For at least twenty years we have had direct experimental proof<sup>1</sup> that the fastest of the  $\alpha$ -particles, or

<sup>1</sup> Bragg, *Phil. Mag.*, VIII (1904), 719, 726; X (1905), 318; XI (1906), 617.

helium atoms, which are ejected by radium, shoot in practically straight lines through as much as 7 cm. of air at atmospheric pressure before being brought to rest. This distance is then called the "range" of these  $\alpha$ -rays. Figs. 14 and 15 show actual photographs of the tracks of such particles. We know too, for the reasons given on p. 139, that these  $\alpha$ -particles do not penetrate the air after the manner of a bullet, namely, by pushing the molecules of air aside, but rather that they actually shoot through all the molecules of air which they encounter. The number of such passages through molecules which an  $\alpha$ -particle would have to make in traversing seven centimeters of air would be about a hundred and thirty thousand.

Further, the very rapid  $\beta$ -particles, or negative electrons, which are shot out by radium have been known for a still longer time to shoot in straight lines through much greater distances in air than 7 cm., and even to pass practically undeflected through appreciable thicknesses of glass or metal.

We saw in chap. vi that the tracks of both the  $\alpha$ - and the  $\beta$ -particles through air could be photographed because they ionize some of the molecules through which they pass. These ions then have the property of condensing water vapor about themselves, so that water droplets are formed which can be photographed by virtue of the light which they reflect. Fig. 17 shows the track of a very high-speed  $\beta$ -ray. A little to the right of the middle of the photograph a straight line can be drawn from bottom to top which will pass through a dozen or so of pairs of specks. These specks are the



FIG. 14



FIG. 15

PHOTOGRAPHS OF THE TRACKS OF  $\alpha$ -PARTICLES  
SHOOTING THROUGH AIR







FIG. 16



FIG. 17

PHOTOGRAPHS OF THE TRACKS OF  $\beta$ -PARTICLES  
SHOOTING THROUGH AIR



water droplets formed about the ions which were produced at these points. Since we know the size of a molecule and the number of molecules per cubic centimeter, we can compute, as in the case of the  $\alpha$ -particle, the number of molecules through which a  $\beta$ -particle must pass in going a given distance. The extraordinary situation revealed by this photograph is that this particular particle shot through on an average as many as 10,000 atoms before it came near enough to an electronic constituent of any one of these atoms to detach it from its system and form an ion. *This shows conclusively that the electronic or other constituents of atoms can occupy but an exceedingly small fraction of the space inclosed within the atomic system. Practically the whole of this space must be empty to an electron going with this speed.*

The left panel in the lower half of the plate (Fig. 16) shows the track of a negative electron of much slower speed, and it will be seen, first, that it ionizes much more frequently, and, secondly, that instead of continuing in a straight line it is deflected at certain points from its original direction. The reason for both of these facts can readily be seen from the considerations on p. 139, which it may be worth while to extend to the case in hand as follows.

If a new planet or other relatively small body were to shoot with stupendous speed through our solar system, the time which it spent within our system might be so small that the force between it and the earth or any other member of the solar system would not have time either to deflect the stranger from its path or to pull the earth out of its orbit. If the speed of the strange

body were smaller, however, the effect would be more disastrous both to the constituents of our solar system and to the path of the strange body, for the latter would then have a much better chance of pulling one of the planets out of our solar system and also a much better chance of being deflected from a straight path itself. The slower a negative electron moves, then, the more is it liable to deflection and the more frequently does it ionize the molecules through which it passes.

This conclusion finds beautiful experimental confirmation in the three panels of the plate opposite this page, for the speed with which X-rays hurl out negative electrons from atoms has long been known to be much less than the speed of  $\beta$ -rays from radium, and the zigzag tracks in these photographs are the paths of these corpuscles. It will be seen that they bend much more often and ionize much more frequently than do the rays shown in Figs. 16 and 17.

But the study of the tracks of the  $\alpha$ -particles (Figs. 14 and 15, opposite p. 190) is even more illuminating as to the structure of the atom. For the  $\alpha$ -particle, being an atom of helium eight thousand times more massive than a negative electron, could no more be deflected by one of the latter in an atom through which it passes than a cannon ball could be deflected by a pea. Yet Figs. 14 and 15 show that toward the end of its path the  $\alpha$ -particle does in general suffer several sudden deflections. Such deflections could be produced only by a very powerful center of force within the atom whose mass is at least comparable with the mass of the helium atom.



FIG. 18



FIG. 19



FIG. 20

PHOTOGRAPHS OF THE TRACKS OF  $\beta$ -PARTICLES EJECTED  
BY X-RAYS FROM MOLECULES OF AIR





These sharp deflections, which occasionally amount to as much as  $150^\circ$  to  $180^\circ$ , lend the strongest of support to the view that the atom consists of a heavy positively charged nucleus about which are grouped enough electrons to render the whole atom neutral. But the fact that in these experiments the  $\alpha$ -particle goes through 130,000 atoms without approaching near enough to this central nucleus to suffer appreciable deflection more than two or three times constitutes the most convincing evidence that this central nucleus which holds the negative electrons within the atomic system occupies an excessively minute volume, just as we computed from the electromagnetic theory of the origin of mass that the positive electron ought to do. Indeed, knowing as he did by direct measurement the speed of the  $\alpha$ -particle, Rutherford, who is largely responsible for the nucleus-atom theory, first computed,<sup>1</sup> with the aid of the inverse square law, which we know to hold between charged bodies of dimensions which are small compared with their distances apart, how close the  $\alpha$ -particle would approach to the nucleus of a given atom like that of gold before it would be turned back upon its course (see Appendix F). The result was in the case of gold, one of the heaviest atoms, about  $10^{-12}$  cm., and in the case of hydrogen, the lightest atom, about  $10^{-13}$  cm. These are merely upper limits for the dimensions of the nuclei.

However uncertain, then, we may feel about the sizes of positive and negative electrons computed from the electromagnetic theory of the origin of the mass, we may regard it as fairly well established by such direct experiments as these that the electronic constituents

<sup>1</sup> *Phil. Mag.*, XXI (1911). 669.

of atoms are as small, in comparison with the dimensions of the atomic systems, as are the sun and planets in comparison with the dimensions of the solar system. Indeed, when we reflect that we can shoot helium atoms by the billion through a thin-walled highly evacuated glass tube without leaving any holes behind, i.e., without impairing in the slightest degree the vacuum or perceptibly weakening the glass, we see from this alone that the atom itself must consist mostly of "hole"; in other words, that an atom, like a solar system, must be an exceedingly loose structure whose impenetrable portions must be extraordinarily minute in comparison with the penetrable portions. The notion that an atom can appropriate to itself all the space within its boundaries to the exclusion of all others is then altogether exploded by these experiments. A particular atom can certainly occupy the same space at the same time as any other atom if it is only endowed with sufficient kinetic energy. Such energies as correspond to the motions of thermal agitation of molecules are not, however, sufficient to enable one atom to penetrate the boundaries of another, hence the seeming impenetrability of atoms in ordinary experiments in mechanics. That there is, however, a portion of the atom which is wholly impenetrable to the alpha particles is definitely proved by experiments of the sort we have been considering; for it occasionally happens that an alpha particle hits this nucleus "head on," and, when it does so, it is turned straight back upon its course. As indicated above, the size of this impenetrable portion, which may be defined as the size of the nucleus, is in no case larger than  $1/10,000$  the diameter of the atom, *and yet there may be contained within*

*it, as will presently be shown, several hundred positive and negative electrons, so that the excessive minuteness of these bodies is established, altogether without reference to any theory as to what they are.*

#### IV. THE NUMBER OF ELECTRONS IN AN ATOM

If it be considered as fairly conclusively established by the experiments just described that an atom consists of a heavy but very minute positively charged nucleus which holds light negative electrons in some sort of a configuration about it, then the number of negative electrons outside the nucleus must be such as to have a total charge equal to the free positive charge of the nucleus, since otherwise the atom could not be neutral.

But the positive charge on the nucleus has been approximately determined as follows: With the aid of the knowledge, already obtained through the determination of  $e$ , of the exact number of atoms in a given weight of a given substance, Sir Ernest Rutherford<sup>1</sup> first computed the chance that a single helium atom in being shot with a known speed through a sheet of gold foil containing a known number of atoms per unit of area of the sheet would suffer a deflection through a given angle. This computation can easily be made in terms of the known kinetic energy and charge of the  $\alpha$ -particle, the known number of atoms in the gold foil, and the unknown charge on the nucleus of the gold atom (see Appendix F). Geiger and Marsden<sup>2</sup> then actually counted in Rutherford's laboratory, by means of the scintillations produced on a zinc-sulphide screen, what

<sup>1</sup> *Phil. Mag.*, XXI (1911), 669-88.

<sup>2</sup> *Ibid.*, XXV (1913), 604.

fraction of, say, a thousand  $\alpha$ -particles, which were shot normally into the gold foil, were deflected through a given angle, and from this observed number and Rutherford's theory they obtained the number of free positive charges on the nucleus of the gold atom.

Repeating the experiment and the computations with foils made from a considerable number of other metals, they found that in every case *the number of free positive charges on the atoms of different substances was approximately equal to half its atomic weight*. This means that the aluminum atom, for example, has a nucleus containing about thirteen free positive charges and that the nucleus of the atom of gold contains in the neighborhood of a hundred. This result was in excellent agreement with the conclusion reached independently by Barkla<sup>1</sup> from experiments of a wholly different kind, namely, experiments on the scattering of X-rays. These indicated that the number of scattering centers in an atom—that is, its number of free negative electrons—was equal to about half the atomic weight. But this number must, of course, equal the number of free positive electrons in the nucleus.

#### V. MOSELEY'S REMARKABLE DISCOVERY

The foregoing result was only approximate. Indeed, there was internal evidence in Geiger and Marsden's work itself that a half was somewhat too high. The answer was made very definite and very precise in 1913 through the extraordinary work of a brilliant young Englishman, Moseley, who, at the age of twenty-seven, had accomplished as notable a piece of research in

<sup>1</sup> *Phil. Mag.*, XXI (1911), 648.

physics as has appeared during the last fifty years. Such a mind was one of the early victims of the world-war. He was shot and killed instantly in the trenches in Gallipoli in the summer of 1915.

Laue in Munich had suggested in 1912 the use of the regular spacing of the molecules of a crystal for the analysis, according to the principle of the grating, of ether waves of very short wave-length, such as X-rays were supposed to be, and the Braggs<sup>1</sup> had not only perfected an X-ray spectrometer which utilized this principle, but had determined accurately the wave-lengths of the X-rays which are characteristic of certain metals. The accuracy with which this can be done is limited simply by the accuracy in the determination of  $e$ , so that the whole new field of exact X-ray spectrometry is made available through our exact knowledge of  $e$ . Moseley's discovery,<sup>2</sup> made as a result of an elaborate and difficult study of the wave-lengths of the characteristic X-rays which were excited when cathode rays were made to impinge in succession upon anticathodes embracing most of the known elements, was that these characteristic wave-lengths of the different elements, or, better, their characteristic frequencies, are related in a very simple but a very significant way. *These frequencies were found to constitute the same sort of an arithmetical progression as do the charges which we found to exist on our oil drops.* It was the square root of the frequencies rather than the frequencies themselves which showed this beautifully simple relationship, but this is an unimportant detail. The significant fact is that, *arranged in the order of increas-*

<sup>1</sup> Bragg, *X-Rays and Crystal Structure*, 1915.

<sup>2</sup> *Phil. Mag.*, XXVI (1912), 1024; XXVII (1914), 703.



*ing frequency of their characteristic X-ray spectra, all the known elements which have been examined constitute a simple arithmetical series each member of which is obtained from its predecessor by adding always the same quantity.*

The plate opposite this page shows photographs of the X-ray spectra of a number of elements whose atomic numbers—that is, the numbers assigned them in Moseley's arrangement of the elements on the basis of increasing X-ray frequency—are given on the left. These photographs were taken by Siegbahn.<sup>1</sup> The distance from the “central image”—in this case the black line on the left—to a given line of the line spectrum on the right is approximately proportional to the wave-length of the rays producing this line. The photographs show beautifully, first, how the atoms of all the elements produce spectra of just the same type, and, secondly, how the wave-lengths of corresponding lines decrease, or the frequencies increase, with increasing atomic number. The photograph on the left shows this progression for the highest frequency rays which the atoms produce, the so-called K series, while the one on the right shows the same sort of a progression for the rays of next lower frequency, namely, those of the so-called L series, which have uniformly from seven to eight times the wave-length of the K series. The plate opposite p. 200 shows some very beautiful photographs taken by De Broglie in Paris<sup>2</sup> in October, 1916. The upper one is the X-ray emission spectrum of tungsten. It consists of general radiations, corresponding to white light, scattered throughout the whole length of the spectrum as a background

<sup>1</sup> *Jahrbuch der Radioaktivität u. Elektronik*, XIII (1916), 326.

<sup>2</sup> *Comptes rendus*, CLXV (1916), 87, 352.



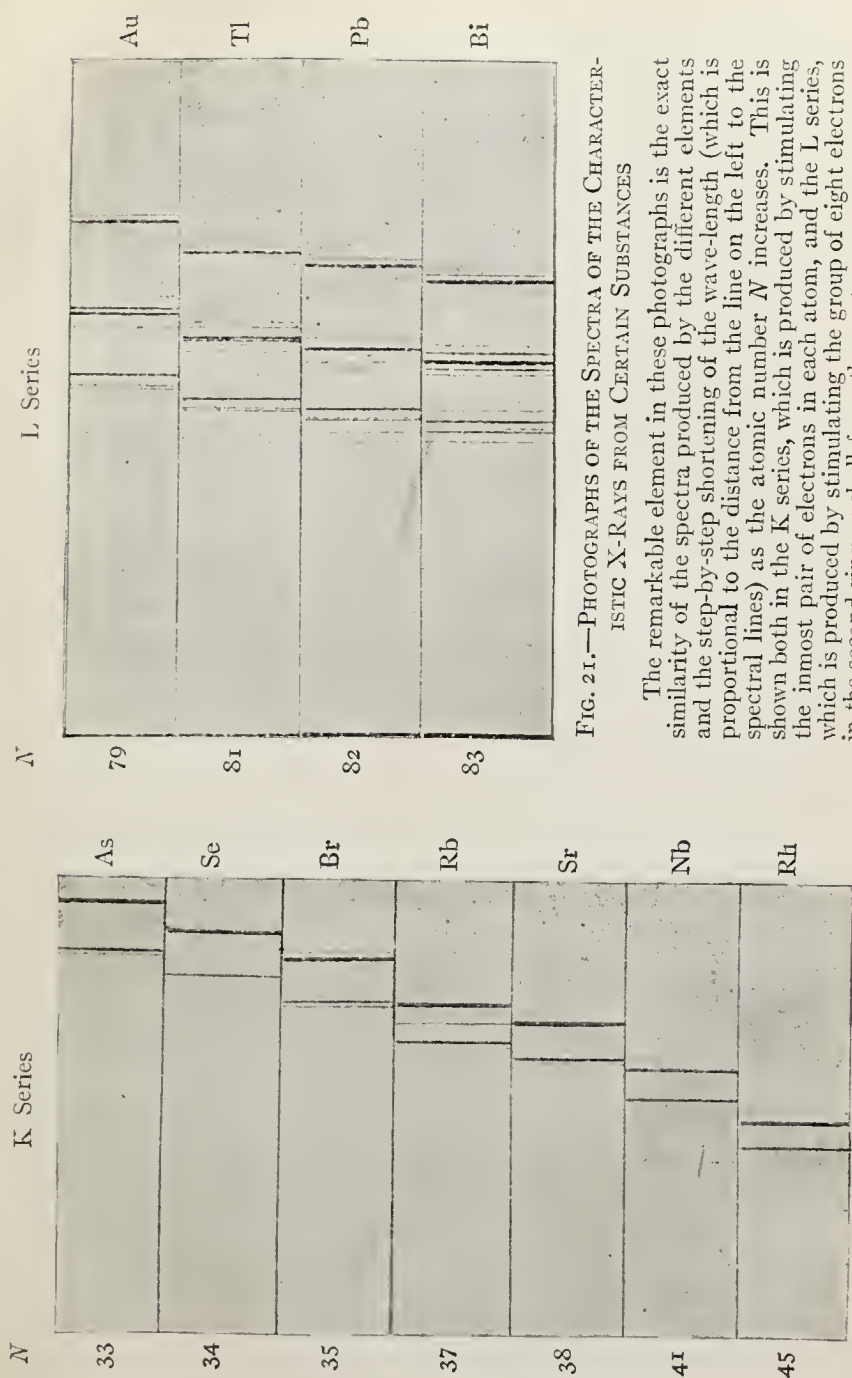


FIG. 21.—PHOTOGRAPHS OF THE SPECTRA OF THE CHARACTERISTIC X-RAYS FROM CERTAIN SUBSTANCES

The remarkable element in these photographs is the exact similarity of the spectra produced by the different elements and the step-by-step shortening of the wave-length (which is proportional to the distance from the line on the left to the spectral lines) as the atomic number  $N$  increases. This is shown both in the K series, which is produced by stimulating the inmost pair of electrons in each atom, and the L series, which is produced by stimulating the group of eight electrons in the second ring or shell from the center.



and superposed upon these two groups of lines. The two K lines are here close to the central image, for the K wave-lengths are here very short, since tungsten has a high atomic number (74). Farther to the right is the L series of tungsten lines which will be recognized because of its similarity to the L series in the plate opposite p. 198. Between the K and the L lines are two absorption edges marked  $\frac{Ag}{K_A}$  and  $\frac{Br}{K_A}$ . The former represents the frequency above which the silver absorbs all the general radiation of tungsten but below which it lets it all through. The latter is the corresponding line for bromine. In a print from a photograph absorption in the plate itself obviously appears as a darkening, transmission as a lightening. Just below is the spectrum obtained by inserting a sheet of molybdenum in the path of the beam, i.e., before the slit of the spectrometer. Absorption in the molybdenum will obviously appear as a lightening, transmission as a darkening. It will be seen that the molybdenum absorbs all the frequencies in the X-ray emission of tungsten higher than a particular frequency and lets through all frequencies lower than this value. This remarkable characteristic of the absorption of X-rays was discovered by Barkla in 1909.<sup>1</sup> The absorption edge at which, with increasing frequency, absorption suddenly begins is very sharply marked. This edge coincides with the highest emission frequency of which molybdenum is theoretically capable, and is a trifle higher than the highest observed emission frequency. De Broglie has measured accurately these critical absorption frequencies for all the heavy elements

<sup>1</sup> Barkla and Sadler, *Phil. Mag.*, XVII (May, 1909), 749.

up to thorium, thus extending the K series from atomic number  $N=60$  where he found it, to  $N=90$ , a notable advance. The two absorption edges characteristic of the silver and the bromine in the photographic plate appear in the same place on all the photographs in which they could appear. The other absorption edges vary from element to element and are characteristic each of its particular element. The way in which this critical absorption edge moves toward the central image as the atomic number increases in the steps Br 35, Mo 42, Ag 47, Cd 48, Sb 51, Ba 56, W 74, Hg 80, is very beautifully shown in De Broglie's photographs all the way up to mercury, where the absorption edge is somewhat inside the shortest of the characteristic K radiations of tungsten. There must be twelve more of these edges between mercury ( $N=80$ ) and uranium ( $N=92$ ) and De Broglie has measured them up to thorium ( $N=90$ ). They become, however, very difficult to locate in this K region of frequencies on account of their extreme closeness to the central image. But the L radiations, which are of seven times longer wave-length, may then be used, and Fig. 23 of the plate opposite this page shows the L-ray absorption edges, of which there are three, as obtained by De Broglie in both uranium and thorium, so that the position in the Moseley table of each element all the way to the heaviest one, uranium, is fixed in this way by direct experiment. Fig. 25 shows the progression of square-root frequencies as it appears from measurements made on the successive absorption edges of De Broglie's photographs and on a particular one of Siegbahn's emission lines. It will be noticed that, in going from bromine (35) to uranium (92), the length of

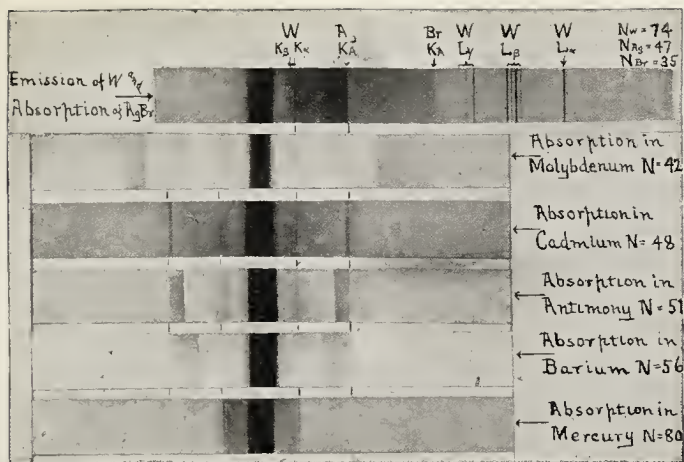


FIG. 22.—X-RAY ABSORPTION SPECTRA, K SERIES

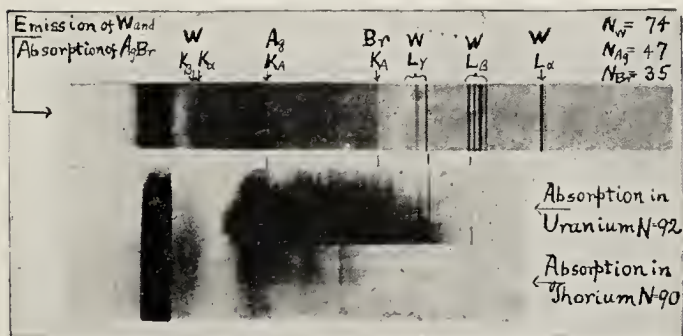


FIG. 23.—X-RAY ABSORPTION SPECTRA, L SERIES



FIG. 24.—HYDROGEN SPECTRUM FROM THE STAR VEGA





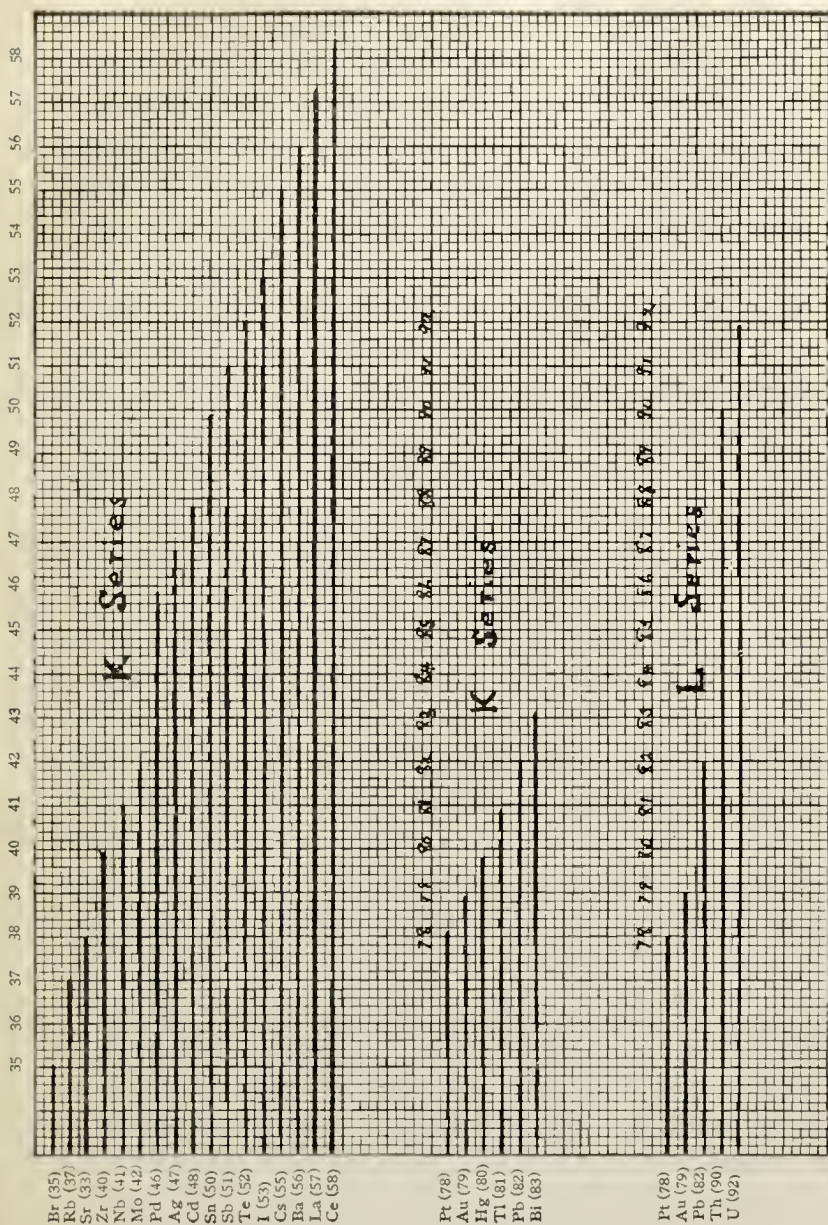


FIG. 25

the step does change by a few per cent. The probable cause of this will be considered later.

According to modern theory an absorption edge appears where the incident energy—which is proportional to the incident frequency—has become just large enough to lift the particular electron which absorbs it entirely out of the atom. If this removed electron should then fall back to its old place in the atom, it would emit in so doing precisely the frequency which was absorbed in the process of removal.

Since these enormously high X-ray frequencies must arise from electrons which fall into extraordinarily powerful fields of force, such as might be expected to exist in the inner regions of the atom close to the nucleus, Moseley's discovery strongly suggests that the charge on this nucleus is produced in the case of each atom by adding some particular invariable charge to the nucleus of the atom next below it in Moseley's table. This suggestion gains added weight when it is found that with one or two trifling exceptions, to be considered later, *Moseley's series of increasing X-ray frequencies is exactly the series of increasing atomic weights*. It also receives powerful support from the following discovery.

Mendeleëff's periodic table shows that the progression of chemical properties among the elements coincides in general with the progression of atomic weights. Now it was pointed out ten years ago that whenever a radioactive substance loses a doubly charged  $\alpha$ -particle it moves two places to the left in the periodic table, while whenever it loses a singly charged  $\beta$ -particle it moves one place to the right,<sup>1</sup> thus showing that the chemical

<sup>1</sup> Soddy, *The Chemistry of the Radioelements*, Part II, 1914.

character of a substance depends upon the number of free positive charges in its nucleus.

One of the most interesting and striking characteristics of Moseley's table is that all the known elements between sodium (atomic number 11, atomic weight 23) and lead (atomic number 82, atomic weight, 207.2) have been fitted into it and there are left but three vacancies within this range. Below sodium there are just 10 known elements, and very recent study<sup>1</sup> of their spectra in the extreme ultra-violet has fixed the place of each in the Moseley progression, though in this region the progression of atomic weights and of chemical properties is also altogether definite and unambiguous. It seems highly probable, then, from Moseley's work that we have already found all except three of the complete series of different types of atoms from hydrogen to lead, i.e., from 1 to 82, of which the physical world is built. From 82 to 92 comes the group of radioactive elements which are continually transmuting themselves into one another, and above 92 (uranium) it is not likely that any elements exist.

That hydrogen is indeed the base of the Moseley series is rendered well-nigh certain by the following simple computation. If we write Moseley's discovery that the square roots of the highest frequencies,  $n_1$ ,  $n_2$ , etc., emitted by different atoms are proportional to the nuclear charges,  $E_1$ ,  $E_2$ , etc., in the following form:

$$\sqrt{\frac{n_1}{n_2}} = \frac{E_1}{E_2} \quad \text{or} \quad \frac{\lambda_2}{\lambda_1} = \frac{E_1^2}{E_2^2} \dots \dots \dots (33)$$

<sup>1</sup> Millikan and Bowen, "Extreme Ultra-Violet Spectra," *Phys. Rev.*, January, 1924.

and substitute for  $\lambda_2$  the observed wave-length of the highest frequency line emitted by tungsten—a wave-length which has been accurately measured and found to be  $0.179 \times 10^{-8}$  cm.; and, further, if we substitute for  $E_2$ , 74, the atomic number of tungsten, and for  $E_1$ , 1, if the Moseley law were exact we should obtain, by solving for  $\lambda_1$ , the wave-length of the highest frequency line which can be emitted by the element whose nucleus contains but one single positive electron. The result of this substitution is  $\lambda_1 = 98.0 \mu\mu$  (millionths millimeters). Now the wave-length corresponding to the highest observed frequency in the ultra-violet series of hydrogen lines recently discovered by Lyman is  $97.4 \mu\mu$  and there is every reason to believe from the form of this series that its convergence wave-length—this corresponds to the highest frequency of which the hydrogen atom is theoretically capable—is  $91.2 \mu\mu$ . The agreement is only approximate, but it is as close as could be expected in view of the lack of exact equality in the Moseley steps. *It is well-nigh certain, then, that this Lyman ultra-violet series of hydrogen lines is nothing but the K X-ray series of hydrogen.* Similarly, it is equally certain that the L X-rays series of hydrogen is the ordinary Balmer series in the visible region, the head of which is at  $\lambda = 365 \mu\mu$ . In other words, hydrogen's ordinary radiations are its X-rays and nothing more.

There is also an M series for hydrogen discovered by Paschen in the ultra-red, which in itself would make it probable that there are series for all the elements of longer wave-length than the L series, and that the complicated optical series observed with metallic arcs are parts of these longer wave-length series. As a



matter of fact, an M series has been found for a considerable group of the elements of high atomic number.

Thus the Moseley experiments have gone a long way toward solving the mystery of spectral lines. They reveal to us clearly and certainly the whole series of elements from hydrogen to uranium, all producing spectra of remarkable similarity, at least so far as the K and L radiations are concerned, but scattered regularly through the whole frequency region, from the ultra-violet, where the K lines for hydrogen are found, all the way up to frequencies  $(92)^2$  or 8,464 times as high. There is scarcely a portion of this whole field which is not already open to exploration. How brilliantly, then, have these recent studies justified the predictions of the spectroscopists that the key to atomic structure lay in the study of spectral lines!

Moseley's work is, in brief, evidence from a wholly new quarter that all these elements constitute a family, each member of which is related to every other member in a perfectly definite and simple way. It looks as if the dream of Thales of Miletus had actually come true and that we have found a primordial element out of which all substances are made, or better two of them. For the succession of steps from one to ninety-two, each corresponding to the addition of an extra free positive charge upon the nucleus, suggests at once that the unit positive charge is itself a primordial element, and this conclusion is strengthened by recently discovered atomic-weight relations. It is well known that Prout thought a hundred years ago that the atomic weights of all elements were exact multiples of the weight of hydrogen, and hence tried to make hydrogen itself the primordial

element. But fractional atomic weights like that of chlorine (35.5) were found, and were responsible for the later abandonment of the theory. Within the past five years, however, it has been shown that, within the limits of observational error, practically all of those elements which had fractional atomic-weights are mixtures of substances, so called *isotopes*, each of which has an atomic weight that is an exact multiple of the unit of the atomic-weight table, so that Prout's hypothesis is now very much alive again.

So far as experiments have now gone, the positive electron, the charge of which is of the same numerical value as that of the negative, *and which is in fact the nucleus of the hydrogen atom*, always has a mass which is about two thousand times that of the negative. In other words, the present evidence is excellent that, to within one part in two thousand, the mass of every atom is simply the mass of the positive electrons contained within its nucleus. Now the atomic weight of helium is four, while its atomic number, the free positive charge upon its nucleus, is only two. The helium atom must therefore contain *inside its nucleus* two negative electrons which neutralize two of these positives and serve to hold together the four positives which would otherwise fly apart under their mutual repulsions. Into that tiny nucleus of helium, then, that infinitesimal speck not as big as a pin point, even when we multiply all dimensions ten billion fold so that the diameter of the helium atom, the orbit of its two outer negatives, has become a yard, into that still almost invisible nucleus there must be packed four positive and two negative electrons.



By the same method it becomes possible to count the exact number of both positive and negative electrons which are packed into the nucleus of every other atom. In uranium, for example, since its atomic weight is 238, we know that there must be 238 positive electrons in its nucleus. But since its atomic number, or the measured number of free unit charges upon its nucleus, is but 92, it is obvious that  $(238 - 92 =)$  146 of the 238 positive electrons in the nucleus must be neutralized by 146 negative electrons *which are also within that nucleus*; and so, in general, *the atomic weight minus the atomic number gives at once the number of negative electrons which are contained within the nucleus of any atom*. That these negative electrons are actually there within the nucleus is independently demonstrated by the facts of radioactivity, for in the radioactive process we find negative electrons, so called  $\beta$ -rays, actually being ejected from the nucleus. They can come from nowhere else, for the chemical properties of the radioactive atom are found to change with every such ejection of a  $\beta$ -ray, and change in chemical character always means change in the free charge contained in the nucleus.

We have thus been able to look with the eyes of the mind, not only inside an atom, a body which becomes but a meter in diameter when looked at through an instrument of ten billion fold magnification, but also inside its nucleus, which, even with that magnification, is still a mere pin point, and to count within it just how many positive and how many negative electrons are there imprisoned, numbers reaching 238 and 146, respectively, in the case of the uranium atom. And let it be remembered, the dimensions of these atomic nuclei are about

one-billionth of those of the smallest object which has ever been seen or can ever be seen and measured in a microscope. From these figures it will be obvious that, for practical purposes, we may neglect the dimensions of electrons altogether and consider them as mere point charges.

But what a fascinating picture of the ultimate structure of matter has been presented by this voyage to the land of the infinitely small! Only two ultimate entities have we been able to see there, namely, positive and negative electrons; alike in the magnitude of their charge but differing fundamentally in mass; the positive being eighteen hundred and forty-five times heavier than the negative; both being so vanishingly small that hundreds of them can somehow get inside a volume which is still a pin point after all dimensions have been swelled ten billion times: the ninety-two different elements of the world determined simply by the difference between the number of positives and negatives which have been somehow packed into the nucleus; all these elements transmutable, ideally at least, into one another by a simple change in this difference. Has nature a way of making these transmutations in her laboratories? She is doing it under our eyes in the radioactive process—a process which we have very recently found is not at all confined to the so-called radioactive elements but is possessed in very much more minute degree by many, if not all, of the elements. Does the process go on in both directions, heavier atoms being continually formed as well as continually disintegrating into lighter ones? Not on the earth so far as we can see. Perhaps in God's laboratories, the stars. Some day we shall be finding out.

Can we on the earth artificially control the process? To a very slight degree we know already how to disintegrate artificially, but not as yet how to build up. As early as 1912, in the Ryerson Laboratory at Chicago, Dr. Winchester and I thought we had good evidence that we were knocking hydrogen out of aluminum and other metals by very powerful electrical discharges *in vacuo*. There may be some doubt about the character of this evidence now. But, certainly, Rutherford has been doing just this for three years past by bombarding the nuclei of atoms with  $\alpha$ -rays. How much farther can we go in this artificial transmutation of the elements? This is one of the supremely interesting problems of modern physics to which there is as yet no answer.

#### VI. THE BOHR ATOM

Thus far nothing has been said as to whether the electrons within the atom are at rest or in motion, or, if they are in motion, as to the character of these motions. In the hydrogen atom, however, which contains, according to the foregoing evidence, but one positive and one negative electron, there is no known way of preventing the latter from falling into the positive nucleus unless centrifugal forces are called upon to balance attractions, as they do in the case of the earth and moon. Accordingly it seems to be necessary to assume that the negative electron is rotating in an orbit about the positive. But such a motion would normally be accompanied by a continuous radiation of energy of continuously increasing frequency as the electron, by virtue of its loss of energy, approached closer and closer to the nucleus. Yet experiment reveals no such behavior, for, so far as we

know, hydrogen does not radiate at all unless it is ionized, or has its negative electron knocked, or lifted, from its normal orbit to one of higher potential energy, and, when it does radiate, it gives rise, not to a continuous spectrum, as the foregoing picture would demand, but rather to a line spectrum in which the frequencies corresponding to the various lines are related to one another in the very significant way shown in the photograph of Fig. 24 and represented by the so-called Balmer-Ritz equation,<sup>1</sup> which has the form

$$\nu = N \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \dots \dots \dots (34)$$

In this formula  $\nu$  represents frequency,  $N$  a constant, and  $n_1$ , for all the lines in the visible region, has the value 2, while  $n_2$  takes for the successive lines the values 3, 4, 5, 6, etc. In the hydrogen series in the infra-red discovered by Paschen<sup>2</sup>  $n_1 = 3$  and  $n_2$  takes the successive values 4, 5, 6, etc. It is since the development of the Bohr theory that Lyman<sup>3</sup> discovered his hydrogen series in the ultra-violet in which  $n_1 = 1$  and  $n_2 = 2, 3, 4$ , etc. Since 1 is the smallest whole number, this series should correspond, as indicated heretofore, to the highest frequencies of which hydrogen is capable, the upper limit toward which these frequencies tend being reached when  $n_1 = 1$  and  $n_2 = \infty$ , that is, when  $\nu = N$ .

<sup>1</sup> Balmer (1885) expressed the formula in wave-lengths. Ritz (1908) first replaced wave-lengths by wave-numbers, or frequencies, and thereby saw his "combination-principle," while Rydberg discovered the general significance of what is now known as the Rydberg constant  $N$ .

<sup>2</sup> Paschen, *Ann. d. Phys.*, XXVII (1908), 565.

<sup>3</sup> *Spectroscopy of the Extreme Ultraviolet*, p. 78.

Guided by all of these facts except the last, Niels Bohr, a young mathematical physicist of Copenhagen, in 1913 devised<sup>1</sup> an atomic model which has had some very remarkable successes. This model was originally designed to cover only the simplest possible case of one

single electron revolving around a positive nucleus. In order to account for the large number of lines which the spectrum of such a system reveals (see Fig. 24), Bohr's first assumption was that the electron may rotate about the nucleus in a whole series of different orbits, as shown in Fig. 26, and

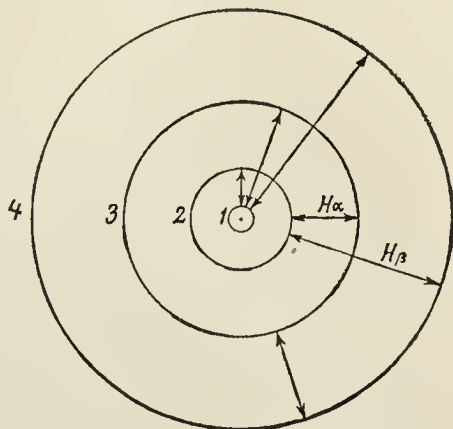


FIG. 26.—The original Bohr model of the hydrogen atom.

that each of these orbits is governed by the well-known Newtonian law, which when mathematically stated takes the form:

$$\frac{eE}{a^2} = (2\pi n)^2 ma \dots \dots \dots (35)$$

in which  $e$  is the charge of the electron,  $E$  that of the nucleus,  $a$  the radius of the orbit,  $n$  the orbital frequency, and  $m$  the mass of the electron. This is merely the assumption that the electron rotates in a circular orbit which is governed by the laws which are known, from

<sup>1</sup> N. Bohr, *Phil. Mag.*, XXVI (1913), 1 and 476 and 857; XXIX (1915), 332; XXX (1915), 394; Sommerfeld, *Atomic Structure and Spectral Lines*. New York: Dutton, 1923.

the work on the scattering of the alpha particles, to hold inside as well as outside the atom. The radical element in it is that it permits the negative electron to maintain this orbit or to persist in this so-called "*stationary state*" without radiating energy even though this appears to conflict with ordinary electromagnetic theory. But, on the other hand, the facts of magnetism<sup>1</sup> and of optics, in addition to the successes of the Bohr theory which are to be detailed, appear at present to lend experimental justification to such an assumption.

Bohr's second assumption is that radiation takes place only when an electron jumps from one to another of these orbits. If  $A_2$  represents the energy of the electron in one orbit and  $A_1$  that in any other orbit, then it is clear from considerations of energy alone that when the electron passes from the one orbit to the other the amount of energy radiated must be  $A_2 - A_1$ ; further, this radiated energy obviously must have some frequency  $\nu$ , and, in view of the experimental work presented in the next chapter, Bohr placed it proportional to  $\nu$ , and wrote:

$$h\nu = A_2 - A_1 \dots \dots \dots (36)$$

$h$  being the so-called Planck constant to be discussed later. It is to be emphasized that this assumption gives no physical picture of the way in which the radiation takes place. It merely states the energy relations which must be satisfied when it occurs. The red hydrogen line  $H_\alpha$  is, according to Bohr, due to a jump from orbit 3 to orbit 2 (Fig. 26), the blue line  $H_\beta$  to a jump from 4 to 2,

<sup>1</sup> Einstein and De Haas, *Verh. der deutsch. phys. Ges.*, XVII (1915), 152; also Barnett, *Phys. Rev.*, VI (1915), 239; also Epstein, *Science*, LVII (1923), 532.



H $\gamma$  to a jump from 5 to 2, etc.; while the Lyman ultra-violet lines correspond to a series of similar jumps into the inmost orbit 1 (see Fig. 26).

Bohr's third assumption is that the various possible circular orbits are determined by assigning to each orbit a kinetic energy  $T$  such that

$$T = \frac{1}{2} \tau h n \dots \dots \dots (37)$$

in which  $\tau$  is a whole number,  $n$  the orbital frequency, and  $h$  is again Planck's constant. This value of  $T$  is assigned so as to make the series of frequencies agree with that actually observed, namely, that represented by the Balmer series of hydrogen.

It is to be noticed that, if circular electronic orbits exist at all, no one of these assumptions is arbitrary. Each of them is merely the statement of the existing *experimental* situation. It is not surprising, therefore, that they predict the sequence of frequencies found in the hydrogen series. They have been purposely made to do so. But they have not been made with any reference whatever to the exact numerical values of these frequencies.

The evidence for the soundness of the conception of non-radiating electronic orbits is to be looked for, then, first, in the success of the constants involved, and, second, in the physical significance, if any, which attaches to the third assumption. If these constants come out right within the limits of experimental error, then the theory of non-radiating electronic orbits has been given the most crucial imaginable of tests, especially if these constants are accurately determinable.

What are the facts? The constant of the Balmer series in hydrogen, that is, the value of  $N$  in equation (34), is known with the great precision attained in all wave-length determinations and is equal to  $3.2888 \times 10^{15}$ . From the Bohr theory it is given by the simplest algebra (Appendix G) as

$$N = \frac{2\pi^2 e^4 m}{h^3} = \frac{2\pi^2 e^5}{h^3 \frac{e}{m}} \dots \dots \dots (38)$$

As already indicated, in 1917 I redetermined<sup>1</sup>  $e$  with an estimated accuracy of one part in 1,000 and obtained for it the value  $4.774 \times 10^{-10}$ . As will be shown in the next chapter, I have also determined  $h$  photo-electrically<sup>2</sup> with an error, in the case of sodium, of no more than one-half of 1 per cent, the value for sodium, upon which I got the most reliable data, being  $6.56 \times 10^{-27}$ . The value found by Duane's X-ray method,<sup>3</sup> which is thought to yield a result correct to one part in 700, is exceedingly close to mine, namely,  $6.555 \times 10^{-27}$ . Substituting this in (38), we get with the aid of Bucherer's value of  $\frac{e}{m}$  ( $1.767 \times 10^7$ ), which is probably correct to 0.1 per cent,  $N = 3.280 \times 10^{15}$ , *which agrees within a fourth of 1 per cent with the observed value*. This agreement constitutes most extraordinary justification of the theory of non-radiating electronic orbits. It demonstrates that the behavior of the negative electron in the hydrogen atom is at least correctly described by the *equation* of a circular non-radiating orbit. If this equation can be

<sup>1</sup> R. A. Millikan, *Phil. Mag.*, XXXIV (1917), 1.

<sup>2</sup> R. A. Millikan, *Phys. Rev.*, VII (1916), 362.

<sup>3</sup> Blake and Duane, *ibid.* (1917), 624.

obtained from some other physical condition than that of an actual orbit, it is obviously incumbent upon those who so hold to show what that condition is. Until this is done, it is justifiable to suppose that the equation of an orbit means an actual orbit.

Again, the radii of the stable orbits for hydrogen are easily found from Bohr's assumptions to take the mathematical form (Appendix G)

$$a = \frac{\tau^2 h^2}{4\pi^2 m e^4} \dots \dots \dots (39)$$

In other words, since  $\tau$  is a whole number, the radii of these orbits bear the ratios 1, 4, 9, 16, 25. If normal hydrogen is assumed to be that in which the electron is in the inmost possible orbit, namely, that for which  $\tau=1$ ,  $2a$ , the diameter of the normal hydrogen *atom*, comes out  $1.1 \times 10^{-8}$ . The best determination for the diameter of the hydrogen *molecule* yields  $2.2 \times 10^{-8}$  in extraordinarily close agreement with the prediction from Bohr's theory.

Further, the fact that normal hydrogen does not absorb at all the Balmer series lines which it emits is beautifully explained by the foregoing theory, since, according to it, normal hydrogen has no electrons in the orbits corresponding to the lines of the Balmer series. Again, the fact that *hydrogen emits its characteristic radiations only when it is ionized or excited* favors the theory that the process of emission is a process of settling down to a normal condition through a series of possible intermediate states, and is therefore in line with the view that a change in orbit is necessary to the act of radiation.

Another triumph of the theory is that the third assumption, devised to fit a purely empirical situation, viz., the observed relations between the frequencies of the Balmer series, is found to have a very simple and illuminating physical meaning and one which has to do with *orbital* motion. It is that all the possible values of the *angular momentum* of the electron rotating about the positive nucleus are exact multiples of a particular value of this angular momentum. Angular momentum then has the property of *atomicity*. Such relationships do not in general drop out of *empirical* formulae. When they do, we usually see in them real interpretations of the formulae—not merely coincidences.

Again, the success of a theory is often tested as much by its adaptability to the explanation of deviations from the behavior predicted by its most elementary form as by the exactness of the fit between calculated and observed results. The theory of electronic orbits has had remarkable successes of this sort. Thus it predicts the Moseley law (33). But this law, discovered afterward, was found inexact, and it should be inexact when there is more than one electron in the atom, as is the case save for H atoms and for such He atoms as have lost one negative charge, and that because of the way in which the electrons influence one another's fields. By taking account of these influences, the inexactnesses in Moseley's law have been very satisfactorily explained.

Another very beautiful quantitative argument for the correctness of Bohr's orbital conception comes from the prediction of a slight difference between the positions in the spectrum of two sets of lines, one due to ionized helium and the other to hydrogen. These two sets of

lines, since they are both due to a single electron rotating about a simple nucleus, ought to be exactly coincident, i.e., they ought to be one and the same set of lines, *if it were not for the fact that the helium nucleus is four times as heavy as the hydrogen nucleus.*

To see the difference that this causes it is only necessary to reflect that, when an electron revolves about a hydrogen nucleus, the real thing that happens is that the two bodies revolve about their common center of gravity. But since the nucleus is two thousand times heavier than the electron, this center is exceedingly close to the hydrogen nucleus.

When, now, the hydrogen nucleus is replaced by that of helium, which is four times as heavy, the common center of gravity is still closer to the nucleus, so that the helium-nucleus describes a much smaller circle than did that of hydrogen. This situation is responsible for a slight but accurately predictable difference in the energies of the two orbits, which should cause the spectral lines produced by electron-jumps to these two different orbits to be slightly displaced from one another.

This predicted slight displacement between the hydrogen and helium lines is not only found experimentally, but the most refined and exact of recent measurements has shown that *the observed displacement agrees with the predicted value to within a small fraction of 1 per cent.*

This not only constitutes excellent evidence for the orbit theory, but it seems to be irreconcilable with a ring-electron theory once favored by some authors, since it requires the mass of the electron to be concentrated at a point.

The next amazing success of the orbit theory came when Sommerfeld<sup>1</sup> showed that the "quantum" principle underlying the Bohr theory ought to demand two different hydrogen orbits corresponding to the second quantum state—second orbit from the nucleus—one a circle and one an ellipse. And by applying the relativity theory to the change in mass of the electron with its change in speed as it moves through the different portions (perihelion and aphelion) of its orbit, he showed that the circular and elliptical orbits should have slightly different energies, and consequently that both the hydrogen and the helium lines corresponding to the second quantum state should be close doublets.

Now *not only is this found to be the fact, but the measured separation of these two doublet lines agrees precisely with the predicted value*, so that this again constitutes extraordinary evidence for the validity of the orbit-conceptions underlying the computation.

In Fig. 27 the two orbits which are here in question are those which are labeled  $2_2$  and  $2_1$ , the large numeral denoting the total quantum number, and the subscript the auxiliary, or *azimuthal*, quantum number which determines the ellipticity of the orbit. The figure is introduced to show the types of stationary orbits which the extended Bohr theory permits. For total quantum number 1 there is but one possible orbit, a circle. For total quantum numbers 2, 3, 4, etc., there are 2, 3, 4, etc., possible orbits, respectively. The ratio of the auxiliary to the total quantum number gives the ratio of the minor and major axes of the ellipse. The fourth quantum

<sup>1</sup> A. Sommerfeld, *Ann. d. Phys.*, III (1916), 1. Also Paschen, *ibid.*, p. 901.



state, for example, has four orbits,  $4_1, 4_2, 4_3, 4_4$ , all of which have the same major axis, but minor axes which increase in the ratios 1, 2, 3, 4 up to equality, in the circle ( $4_4$ ), with the major axis. It is this multiplicity of orbits which predicts with beautiful accuracy the "fine-structure" of all of the lines due to atomic hydrogen and to helium.

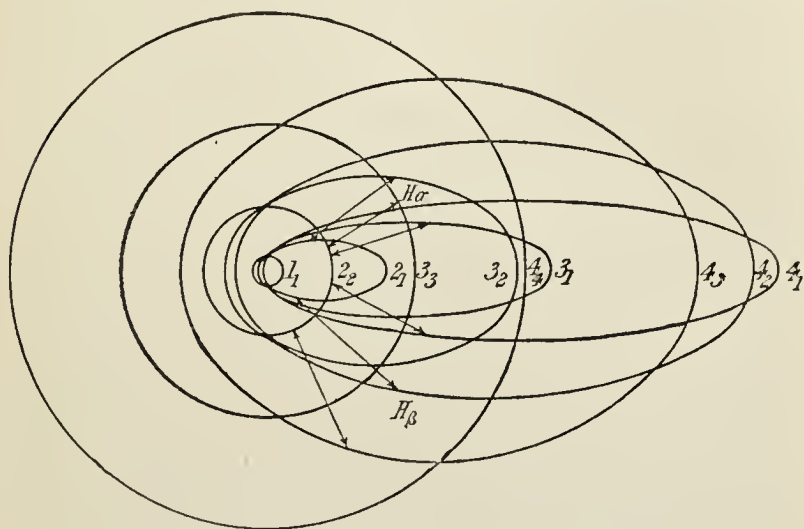


FIG. 27.—Bohr-Sommerfeld model of the hydrogen atom with stationary orbits corresponding to principal quantum numbers and auxiliary or azimuthal quantum numbers.

The next quantitative success of the Bohr theory came when Epstein,<sup>1</sup> of the California Institute, applied his amazing grasp of orbit theory to the exceedingly difficult problem of computing the perturbations in electron orbits, and hence the change in energy of each, due to exciting hydrogen and helium atoms to radiate in an electrostatic field. He thus predicted the whole complex character of what we call the "Stark effect,"

<sup>1</sup> P. Epstein, *ibid.*, L (1916), 489.

showing just how many new lines were to be expected and where each one should fall, and then *the spectroscope yielded, in practically every detail, precisely the result which the Epstein theory demanded.*

Another quantitative success of the orbit theory is one which Mr. I. S. Bowen and the author,<sup>1</sup> at the California Institute, have just brought to light. Through creating what we call "hot sparks" in extreme vacuum we have succeeded in stripping in succession, 1, 2, 3, 4, 5, and 6 of the valence, or outer, electrons from the atoms studied. In going from lithium, through beryllium, boron and carbon to nitrogen, we have thus been able to work with stripped atoms of all these substances.

Now these stripped atoms constitute structures which are all exactly alike save that the fields in which the single electron is radiating as it returns toward the nucleus increase in the ratios 1, 2, 3, 4, 5, as we go from stripped lithium to stripped nitrogen. *We have applied the relativity-doublet formula, which, as indicated above, Sommerfeld had developed for the simple nucleus-electron system found in hydrogen and ionized helium, and have found that it not only predicts everywhere the observed doublet-separation of the doublet-lines produced by all these stripped atoms, but that it enables us to compute how many electrons are in the inmost, or K shell, screening the nucleus from the radiating electron. This number comes out just 2, as we know from radioactive and other data that it should.* (See inset photograph, Fig. 37, following Fig. 36, opposite p. 260.)

Further, when we examine the spectra due to the stripped atoms of the group of elements from sodium

<sup>1</sup> See *Phys. Rev.*, July, 1924.

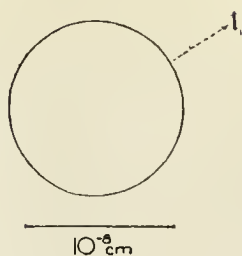
to sulphur, one electron having been knocked off from sodium, two from magnesium, three from aluminum, four from silicon, five from phosphorus, and six from sulphur, we ought to find that the number of screening electrons in the two inmost shells combined is  $2+8=10$ , and it does come out 10, precisely as predicted, and all this through the simple application of the principle of change of mass with speed in elliptical electronic orbits of the type shown in Fig. 27.

The physicist has thus piled Ossa upon Pelion in his quantitative proof of the existence of electronic orbits within atoms. About the *shapes* of these orbits he has some little information (Fig 27) but about their *orientations* he is as yet pretty largely in the dark. The diagrams<sup>1</sup> on the accompanying pages, Figs. 28, 29, and 31, represent hypothetical conceptions, due primarily to Bohr, of the electronic orbits in a group of atoms. Since, however, these orbits are some sort of space configurations, the accompanying plane diagrams are merely schematic. They may be studied in connection with Fig 27, Table XIV, and Bohr's diagram<sup>2</sup> of the periodic system of the elements shown in Fig. 30. These contain the most essential additions which Bohr made in 1922 and 1923 to the simple theory developed in 1913.

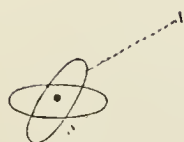
The most characteristic feature of these additions is the conception of the penetration, in the case of the less simple atoms, of electrons in highly elliptical orbits into the region inside the shells of lower quantum number.

<sup>1</sup> These appeared in an article by Kramers in *Naturwissenschaften*, 1923.

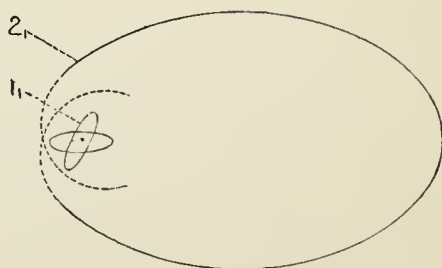
<sup>2</sup> Bohr and Coster, *Zeit. f. Physik*, XII (1923), 344.



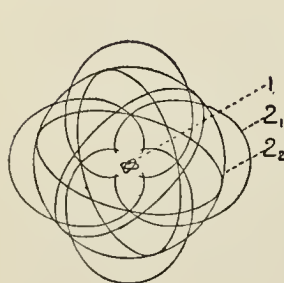
HYDROGEN (1)



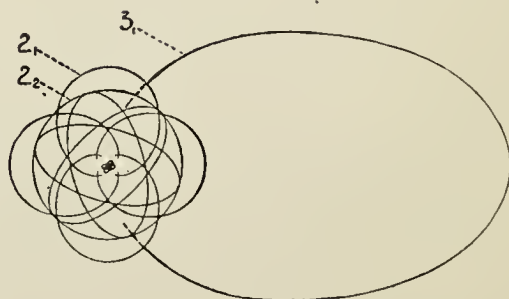
HELIUM (2)



LITHIUM (3)



NEON (10)

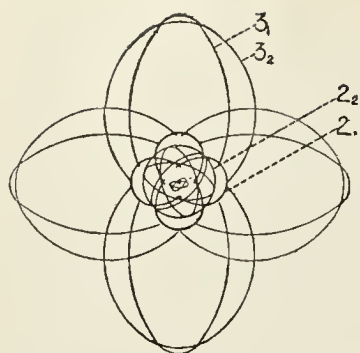


SODIUM (11)

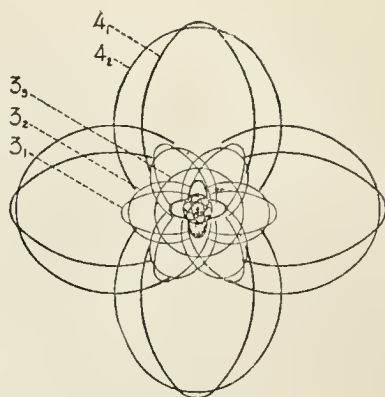
FIG. 28.—Hypothetical atomic structures

This gives, so Bohr believes, these penetrating electron-orbits in some cases a smaller mean potential energy, and therefore a higher stability, than some of the orbits corresponding to the smaller quantum numbers.

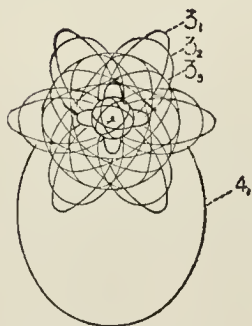
A glance at the group of elements beginning with argon, the last element in shell 3, in both Table XIV and Fig. 30, will make clear the meaning of this statement. The fourth column of Table XIV shows that Bohr assigns to argon four very elliptical orbits of shape  $3_1$  and four of shape  $3_2$ . Glancing down the same column to copper, or lower, one sees that there are eighteen possible third-shell orbits, namely, six of shape  $3_1$ , six of shape  $3_2$ , and six of shape  $3_3$ , i.e., there are in the third shell in argon ten unfilled orbits. But when a new electron is added, as we pass from argon to potassium, it goes, according to Bohr, into the  $4_1$  orbit, thus giving potassium univalent properties like lithium and sodium (see Fig. 28). Similarly, calcium is shown in Table XIV as taking its two extra electrons into its  $4_1$  orbits. But as now the nuclear charge gets stronger and stronger with increasing atomic number, the empty third-shell orbits gain in stability over the fourth-shell ones, and a stage of reconstruction sets in with scandium (Fig. 30) and continues down to copper, all the added electrons now going *inside* to fill the ten empty orbits in the third shell, with the result that the chemical properties, which depend on the outer or valence electrons, do not change much while this is going on. With copper (see Table XIV) the eighteen third-shell orbits are completely filled and one electron is in the  $4_1$  orbit (see also Fig. 29), and from there down to krypton the chemical properties progress normally much as they do from Mg to Ar.



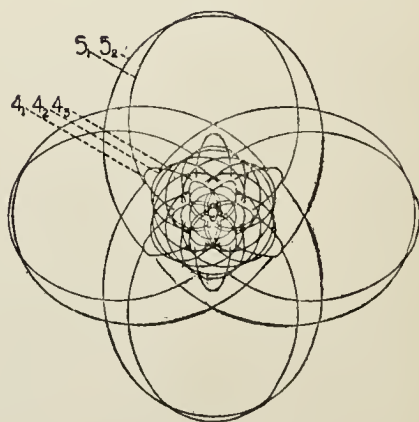
ARGON (18)



KRYPTON (36)



COPPER (29)



XENON (54)

FIG. 29.—Hypothetical atomic structures



Precisely the same procedure is repeated in the fifth period of eighteen elements between krypton and xenon, the rare-earth group which intervenes between strontium (Sr) and silver (Ag) corresponding to the elements in which, with increasing atomic number, the added electrons are filling up the empty orbits in the fourth shell instead of going into what is now the outer or fifth shell (see Table XIV).

Now in considering the sixth period of thirty-two elements from xenon (Xe) to niton (Nt), a glance at Table XIV shows that the fourth shell in xenon contained only eighteen electrons, whereas in niton there are thirty-two, i.e., there are fourteen unfilled orbits in xenon in the fourth shell; and a similar glance at the fifth shell shows  $18-8=10$  vacant orbits there. The first two elements in this group, viz., caesium (Cs) and barium (Ba), take the added electrons in  $6s$  orbits, then the electrons begin to go inside until gold is reached, when the fourth and fifth shells become full and from gold (Au) to niton (Nt), as the added electrons go to the outer shell, the chemical properties again progress as from sodium to argon, or from copper to krypton.

It will be noticed that in Fig. 30 element 72 is hafnium, the element discovered in 1923 by Coster and Hevesy<sup>1</sup> by means of X-ray analysis. It is because its chemical properties resemble so closely those of zirconium that it had not been found earlier by chemical means. Hevesy estimates that it represents one one hundred-thousandth of the earth's crust, which makes it more plentiful than lead or tin.

<sup>1</sup> Coster and Hevesy, *Nature*, III (1923), 79; *Ber. d. chem. Ges.*, LVI (1923), 1503.

1 H	3 Li	11 Na	19 K	27 Sc	37 Rb	55 Cs	87 -
2 He	4 Be	12 Mg	20 Ca	22 Ti	38 Sr	56 Ba	88 Ra
	5 B	13 Al	21 Sc	23 V	39 Y	57 La	89 Ac
	6 C	14 Si	24 Cr	26 Fe	40 Zr	58 Ce	90 Th
	7 N	15 P	25 Mn	27 Co	41 Nb	59 Pr	91 Pa
	8 O	16 S	28 Ni	29 Cu	42 Mo	60 Nd	92 U
	9 F	17 Cl	30 Zn	31 Ga	43 -	61 -	
	10 Ne	18 Ar	32 Ge	33 As	44 Ru	62 Sm	
			34 Se	35 Br	45 Rh	63 Eu	
			36 Kr	37 Rb	46 Pd	64 Gd	
				38 Sr	47 Ag	65 Tb	
				39 Y	48 Cd	66 Dy	
				40 Zr	49 In	67 Ho	
				41 Nb	50 Sn	68 Er	
				42 Mo	51 Sb	69 Tm	
				43 -	52 Te	70 Yb	
				44 Ru	53 I	71 Lu	
				45 Rh	54 Xe	72 Hf	
				46 Pd		73 Ta	
				47 Ag		74 W	
				48 Cd		75 -	
				49 In		76 Os	
				50 Sn		77 Ir	
				51 Sb		78 Pt	
				52 Te		79 Au	
				53 I		80 Hg	
				54 Xe		81 Tl	
						82 Pb	
						83 Bi	
						84 Po	
						85 -	
						86 Rn	113 -

FIG. 30.—Bohr's form of the periodic table, the most illuminating thus far devised. The elements which are in process of orbital reconstruction, because of the passage of electrons into thus far unfilled inner quantum orbits, are inclosed in frames. Lines connect elements which have similar properties.

TABLE XIV

NUMBER OF ELECTRONS IN DIFFERENT  $n_k$  ORBITS

Period	Z	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f	6s 6p 6d 6f	7s 7p
1...	1 H 2 He	1						
2...	3 Li 4 Be 5 B	2	1 2 2(1)					
	10 Ne	2	4 4					
3...	11 Na 12 Mg 13 Al	2	4 4	1 2 2 1				
	18 A	2	4 4	4 4				
4...	19 K 20 Ca 21 Sc 22 Ti	2	4 4	4 4	1 2 (2) (2)			
	29 Cu 30 Zn 31 Ga	2	4 4	6 6 6 6 6 6 6 6 6	1 2 2 1			
	36 Kr	2	4 4	6 6 6	4 4			
5...	37 Rb 38 Sr 39 Y 40 Zr	2	4 4	6 6 6	4 4 4 4 4 4 1 4 4 2	1 2 (2) (2)		
	47 Ag 48 Cd 49 In	2	4 4	6 6 6	6 6 6 6 6 6 6 6 6	1 2 2 1		
	54 Xe	2	4 4	6 6 6	6 6 6	4 4		
6...	55 Cs 56 Ba 57 La 58 Ce 59 Pr	2	4 4	6 6 6	6 6 6 6 6 6 6 6 6 6 6 6 1 6 6 6 2	4 4 4 4 4 4 1 4 4 1 4 4 1	1 2 (2) (2) (2)	
	71 Lu 72 Hf	2	4 4	6 6 6	8 8 8 8 8 8 8 8	4 4 1 4 4 2	(2) (2)	
	79 Au 80 Hg 81 Tl	2	4 4	6 6 6	8 8 8 8 8 8 8 8 8 8 8 8	6 6 6 6 6 6 6 6 6	1 2 2 1	
	86 Pt	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
7...	87 — 88 Ra 89 Ac 90 Th	2	4 4	6 6 6	8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	6 6 6 6 6 6 6 6 6 6 6 6	4 4 4 4 4 4 1 4 4 2	1 (2) (2) (2)
	118 (?)	2	4 4	6 6 6	8 8 8 8	8 8 8 8	6 6 6	4 4

The seventh period begins (Fig. 30) with an unknown element of atomic number 87, which, with its single  $7_1$  orbit, should have a valency of 1, then passes to radium with its two  $7_1$  orbits (see Fig. 31) and valency 2, and breaks off suddenly with uranium because the *nucleus* has here become unstable.

It should be clearly understood that the detailed theory as here presented, and above all the models of complicated atoms, are to a very considerable degree hypothetical and speculative. But it is highly probable that they give a more or less correct *general* picture of the way electrons behave in atoms. So far as the general conception of orbits which behave in the main, especially in the simpler atoms, in accordance with the Bohr assumptions, is concerned, if the test of truth in a physical theory is large success both in the prediction of new relationships and in correctly and exactly accounting for old ones, the theory of non-radiating orbits is one of the well-established truths of modern physics. For the present at least it is truth, and no other theory of atomic structure need be considered until it has shown itself able to approach it in fertility. I know of no competitor which is as yet even in sight.

I am well aware that the facts of organic chemistry seem to demand that the valence electrons be grouped in certain definite equilibrium positions about the periphery of the atom, and that at first sight this demand appears difficult to reconcile with the theory of electronic orbits. But a little reflection shows that there is here no necessary clash. With a suitable *orientation* of orbits, these localized valencies of chemistry are about as easy to reconcile with an orbit theory as with a fixed electron

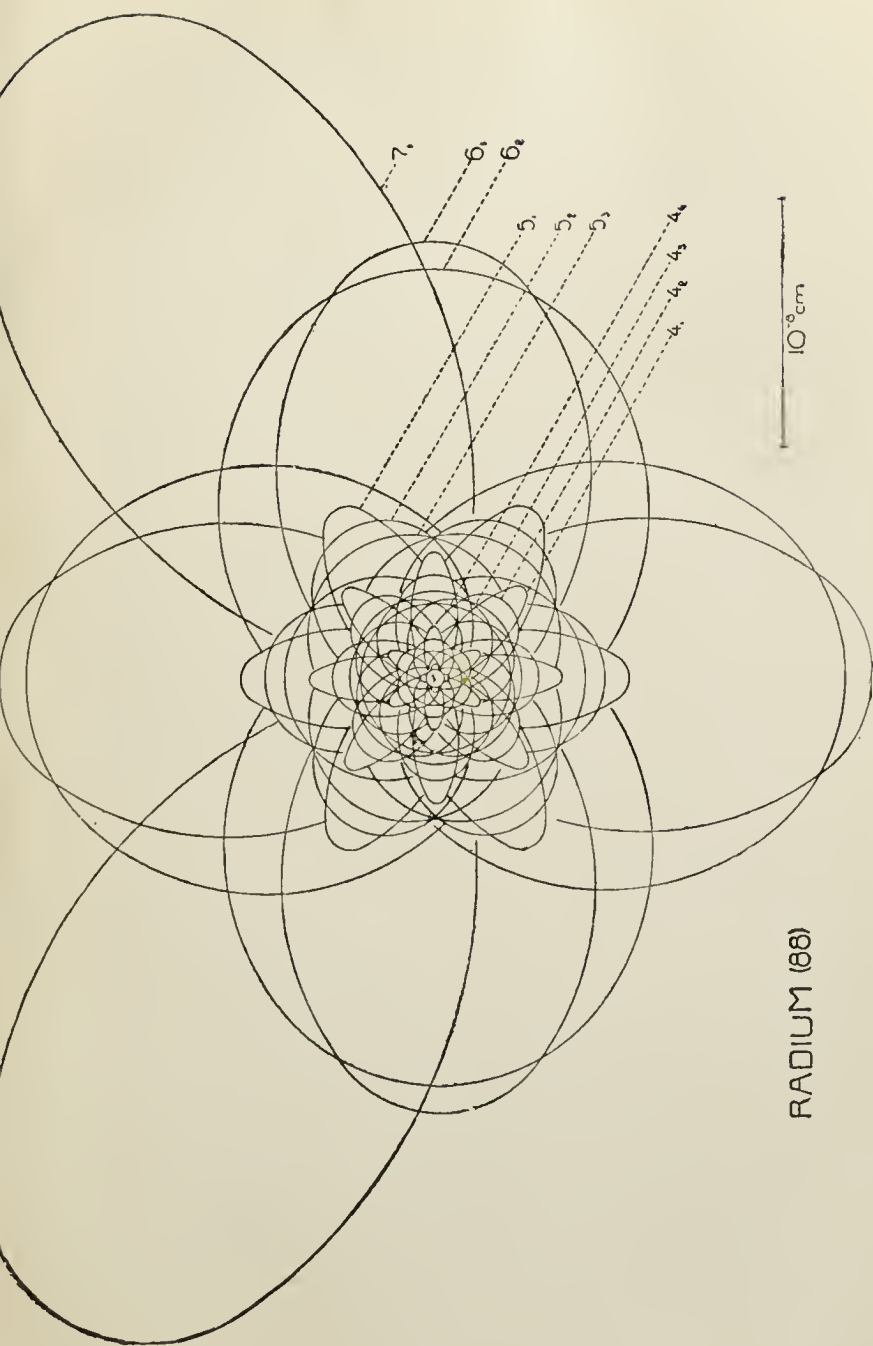


FIG. 31.—Hypothetical structure of the radium atom

theory. It is only for *free atoms* that spectroscopic evidence has forced us to build up orbit pictures of the foregoing sort. When atoms unite into molecules, or into solid bodies, these orbits will undoubtedly be very largely readjusted under the mutual influence of the two or more nuclei which are now acting simultaneously upon them.

It has been objected, too, that the Bohr theory is not a radiation theory because it gives us no picture of the mechanism of the production of the frequency  $\nu$ . This is true, and therein lies its strength, just as the strength of the first and second laws of thermodynamics lies in the fact that they are true irrespective of a mechanism. The Bohr theory is a theory of atomic structure; it is not a theory of radiation, for it merely states what energy relations must exist when radiation, whatever its mechanism, takes place. It is the first attempt to determine in the light of well-established experimental facts what the electrons inside the atom are doing, and as such a first attempt it must be regarded as, thus far, a success, though it has by no means got beyond the hypothetical stage. Its chief difficulty arises from the apparent contradiction involved in a non-radiating electronic orbit, and there appears to be no solution to this difficulty save in the denial of the *universal* applicability of the classical electromagnetic laws. But why assume the universal applicability of these laws, even in the hearts of atoms, when this is the first opportunity which we have had to test them out in the region of the infinitely small?

There is one other very important relation predicted by the Bohr theory and beautifully verified by experiment, but not involving at all its orbital feature. The



frequency value of the inmost, or K level, can be exactly determined by measuring the K absorption edge so beautifully shown on the De Broglie photographs opposite p. 200. Let us call this frequency  $\nu_{KA}$ . Similarly, to each orbit in the second or  $L$  quantum state, there corresponds a definite absorption edge  $\nu_{LA}$ . Two of these are shown clearly in Fig. 23. The difference between the K absorption frequency and each  $L$  absorption frequency should obviously, according to Bohr, correspond exactly to the frequency  $\nu_{Ka}$  of an *emission* line in the K X-ray spectrum, i.e.,

$$\nu_{KA} - \nu_{LA} = \nu_{Ka} \dots\dots\dots (40)$$

This so-called Kossel relation is of course applicable to all X-ray and optical spectra. Indeed, in the latter field it appeared before the Bohr theory under the name of the "Ritz combination principle." It has been one of the most important keys to the unlocking of the meaning of spectra and the revealing of *atomic structure*.

## CHAPTER X

### THE NATURE OF RADIANT ENERGY

The problems thus far discussed have all been in the domain of molecular physics, but the discovery and measurement of the electron have also exerted a powerful influence upon recent developments in the domain of ether physics. These developments are of extraordinary interest and suggestiveness, but they lead into regions in which the physicist sees as yet but dimly—indeed even more dimly than he thought he saw twenty years ago.

But while the beauty of a problem solved excites the admiration and yields a certain sort of satisfaction, it is after all the unsolved problem, the quest of the unknown, the struggle for the unattained, which is of most universal and most thrilling interest. I make no apologies, therefore, for introducing in this chapter one of the great unsolved problems of modern physics, nor for leaving it with but the vaguest of suggestions toward a solution.

#### I. THE CORPUSCULAR AND THE ETHER THEORIES OF RADIATION

The newest of the problems of physics is at the same time the oldest. For nothing is earlier in the experiences either of the child or of the race than the sensation of receiving light and heat from the sun. But how does light get to us from the sun and the stars through the empty interstellar spaces? The Greeks answered this query very simply and very satisfactorily from the standpoint of people who were content with plausible explanations

but had not yet learned perpetually to question nature experimentally as to the validity or invalidity of a conclusion. They said that the sun and all radiators of light and heat must shoot off minute corpuscles whose impact upon the eye or skin produces the sensations of light and warmth.

This corpuscular theory was the generally accepted one up to 1800 A.D. It was challenged, it is true, about 1680 by the Dutch physicist Huygens, who, starting with the observed phenomena of the transmission of water waves over the surface of a pond or of sound waves through the air, argued that light might be some vibratory disturbance transmitted by some medium which fills all interstellar space. He postulated the existence of such a medium, which was called the luminiferous or light-bearing ether.

Partly no doubt because of Newton's espousal of the corpuscular theory, the ether or wave theory gained few adherents until some facts of interference began to appear about 1800 which baffled explanation from the standpoint of the corpuscular theory, but which were easily handled by its rival. During the nineteenth century the evidence became stronger and stronger, until by its close the corpuscular theory had been completely eliminated for four different reasons: (1) The facts of interference were not only found inexplicable in terms of it, but they were completely predicted by the wave theory. (2) The fact that the speed of propagation of light was experimentally found to be greater in air than in water was in accord with the demands of the ether theory, but directly contrary to the demands of the corpuscular theory. (3) Wireless waves had appeared and had been shown

to be just like light waves save for wave-length, and they had been found to pass over continuously, with increasing wave-length, into static electrical fields such as could not apparently be explained from a corpuscular point of view. (4) The speed of light had been shown to be independent of the speed of the source as demanded by the ether theory and denied by the corpuscular theory.

By 1900, then, the ether theory had become apparently impregnably intrenched. A couple of years later it met with some opposition of a rather ill-considered sort, as it seems to me, from a group of extreme advocates of the relativity theory, but this theory is now commonly regarded, I think, as having no bearing whatever upon the question of the existence or non-existence of a luminiferous ether. For such an ether was called into being solely for the sake of furnishing a carrier for electromagnetic waves, and it obviously stands or falls with the existence of such waves *in vacuo*, and this has never been questioned by anyone so far as I am aware.

## II. DIFFICULTIES CONFRONTING THE WAVE THEORY

Up to 1903, then, the theory which looked upon an electromagnetic wave as a disturbance which originated at some point in the ether at which an electric charge was undergoing a change in speed, and was propagated from that point outward as a spherical wave or pulse, the total energy of the disturbance being always spread uniformly over the wave front, had met with no serious question from any source. Indeed, it had been extraordinarily successful, not only in accounting for all the known facts, but in more than one instance in predicting new ones. The first difficulty appeared after the discovery of the

electron and in connection with the relations of the electron to the absorption or emission of such electromagnetic waves. It was first pointed out in 1903 by Sir J. J. Thomson in his Silliman lectures at Yale. It may be stated thus:

X-rays unquestionably pass over all but an exceedingly minute fraction, say one in a thousand billion, of the atoms contained in the space traversed without spending any energy upon them or influencing them in any observable way. But here and there they find an atom from which, as is shown in the photographs opposite p. 192, they hurl a negative electron with enormous speed. This is the most interesting and most significant characteristic of X-rays, and one which distinguishes them from the  $\alpha$ - and  $\beta$ -rays just as sharply as does the property of non-deviability in a magnetic field; for Figs. 14 and 15 and the plate opposite p. 190 show that neither  $\alpha$ - nor  $\beta$ -rays ever eject electrons from the atoms through which they pass, with speeds comparable with those produced by X-rays, else there would be new long zigzag lines branching out from points all along the paths of the  $\alpha$ - and  $\beta$ -particles shown in these photographs.

But this property of X-rays introduces a serious difficulty into the ether theory. For if the electric intensity in the wave front of the X-ray is sufficient thus to hurl a corpuscle with huge energy from one particular atom, why does it not at least detach corpuscles from all of the atoms over which it passes?

Again when ultra-violet light falls on a metal it, too, like X-rays, is found to eject negative electrons. This phenomenon of the emission of electrons under the

influence of light is called the photo-electric effect. Lenard<sup>1</sup> first made the astonishing discovery that the energy of ejection of the electron is altogether independent of the intensity of the light which causes the ejection, no matter whether this intensity is varied by varying the distance of the light or by introducing absorbing screens. I have myself<sup>2</sup> subjected this relation to a very precise test and found it to hold accurately. Furthermore, this sort of independence has also been established for the negative electrons emitted by both X- and  $\gamma$ -rays.

Facts of this sort are evidently difficult to account for on any sort of a spreading-wave theory. But it will be seen that they lend themselves to easy interpretation in terms of a corpuscular theory, for if the energy of an escaping electron comes from the absorption of a light-corpuscle, then the energy of emission of the ejected electron ought to be independent of the distance of the source, as it is found to be, and furthermore corpuscular rays would hit but a very minute fraction of the atoms contained in the space traversed by them. This would explain, then, both the independence of the energy of emission upon intensity and the smallness of the number of atoms ionized.

In view, however, of the four sets of facts mentioned above, Thomson found it altogether impossible to go back to the old and exploded form of corpuscular theory for an explanation of the new facts as to the emission of electrons under the influence of ether waves. He accordingly attempted to reconcile these troublesome new facts with the wave theory by assuming a fibrous structure in the ether and picturing all electromagnetic

<sup>1</sup> *Ann. d. Phys.* (4), VIII (1902), 149.

<sup>2</sup> *Phys. Rev.*, I (1913), 73.



energy as traveling along Faraday lines of force conceived of as actual strings extending through all space. Although this concept, which we shall call the ether-string theory, is like the corpuscular theory in that the energy, after it leaves the emitting body, remains localized in space, and, when absorbed, is absorbed as a whole, yet it is after all essentially an ether theory. For in it the speed of propagation is determined by the properties of the medium—or of space, if one prefers a mere change in name—and has nothing to do with the nature or condition of the source. Thus the last three of the fatal objections to a corpuscular theory are not here encountered. As to the first one, no one has yet shown that Thomson's suggestion is reconcilable with the facts of interference, though so far as I know neither has its irreconcilability been as yet absolutely demonstrated.

But interference aside, all is not simple and easy for Thomson's theory. For one encounters serious difficulties when he attempts to visualize the universe as an infinite cobweb whose threads never become tangled or broken however swiftly the electrical charges to which they are attached may be flying about.

### III. EINSTEIN'S QUANTUM THEORY OF RADIATION

Yet the boldness and the difficulties of Thomson's "ether-string" theory did not deter Einstein<sup>1</sup> in 1905 from making it even more radical. In order to connect it up with some results to which Planck of Berlin had been led in studying the facts of black-body radiation, Einstein assumed that the energy emitted by any radiator not only kept together in bunches or quanta as it traveled

*Ann. d. Phys.* (4), XVII (1905), 132; XX (1906), 199.

through space, as Thomson had assumed it to do, but that a given source could emit and absorb radiant energy only in units which are all exactly equal to  $h\nu$ ,  $\nu$  being the natural frequency of the emitter and  $h$  a constant which is the same for all emitters.

I shall not attempt to present the basis for such an assumption, for, as a matter of fact, it had almost none at the time. But whatever its basis, it enabled Einstein to predict at once that the energy of emission of electrons under the influence of light would be governed by the equation

$$\frac{1}{2}mv^2 = Ve = h\nu - p \dots\dots\dots (41)$$

in which  $h\nu$  is the energy absorbed by the electron from the light wave or light quantum, for, according to the assumption it was the whole energy contained in that quantum,  $p$  is the work necessary to get the electron out of the metal, and  $\frac{1}{2}mv^2$  is the energy with which it leaves the surface—an energy evidently measured by the product of its charge  $e$  by the potential difference  $V$  against which it is just able to drive itself before being brought to rest.

At the time at which it was made this prediction was as bold as the hypothesis which suggested it, for at that time there were available no experiments whatever for determining anything about how the positive potential  $V$  necessary to apply to the illuminated electrode to stop the discharge of negative electrons from it under the influence of monochromatic light varied with the frequency  $\nu$  of the light, or whether the quantity  $h$  to which Planck had already assigned a numerical value appeared at all in connection with photo-electric discharge. We

are confronted, however, by the astonishing situation that after ten years of work at the Ryerson Laboratory (1904-15) and elsewhere upon the discharge of electrons by light this equation of Einstein's was found to predict accurately all of the facts which had been observed.

#### IV. THE TESTING OF EINSTEIN'S EQUATION

The method which was adopted in the Ryerson Laboratory for testing the correctness of Einstein's equation involved the performance of so many operations upon the highly inflammable alkali metals in a vessel which was freed from the presence of all gases that it is not inappropriate to describe the experimental arrangement as a machine-shop *in vacuo*. Fig. 32 shows a photograph of the apparatus, and Fig. 33 is a drawing of a section which should make the necessary operations intelligible.

One of the most vital assertions made in Einstein's theory is that the kinetic energy with which monochromatic light ejects electrons from any metal is proportional to the frequency of the light, i.e., if violet light is of half the wave-length of red light, then the violet light should throw out the electron with twice the energy imparted to it by the red light. In order to test whether any such linear relation exists between the energy of the escaping electron and the light which throws it out it was necessary to use as wide a range of frequencies as possible. This made it necessary to use the alkali metals, sodium, potassium, and lithium, for electrons are thrown from the ordinary metals only by ultra-violet light, while the alkali metals respond in this way to any waves shorter than those of the red, that is,

they respond throughout practically the whole visible spectrum as well as the ultra-violet spectrum. Cast cylinders of these metals were therefore placed on the wheel *W* (Fig. 33) and fresh clean surfaces were obtained by cutting shavings from each metal in an excellent vacuum with the aid of the knife *K*, which was operated

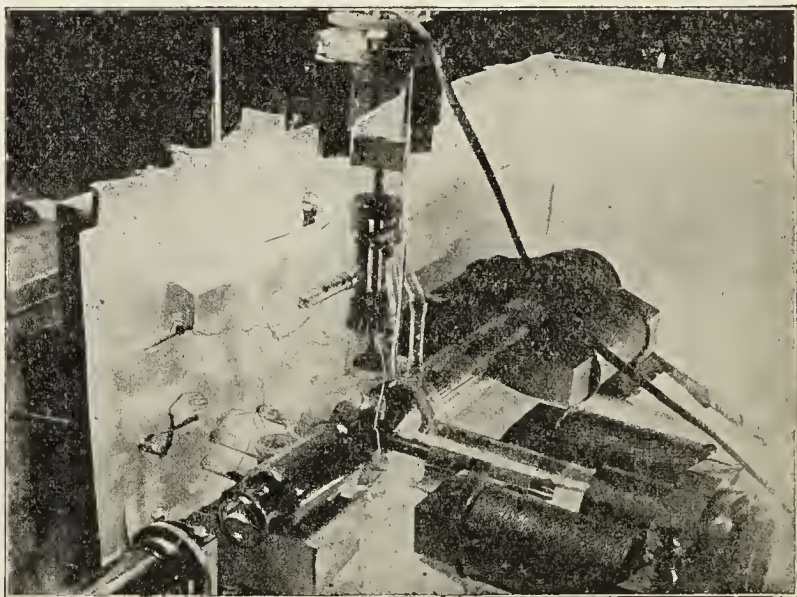


FIG. 32

by an electromagnet *F* outside the tube. After this the freshly cut surface was turned around by another electromagnet until it was opposite the point *O* of Fig. 33 and a beam of monochromatic light from a spectrometer was let in through *O* and allowed to fall on the new surface. The energy of the electrons ejected by it was measured by applying to the surface a positive potential just strong enough to prevent any of the discharged electrons from

reaching the gauze cylinder opposite (shown in dotted lines) and thus communicating an observable negative

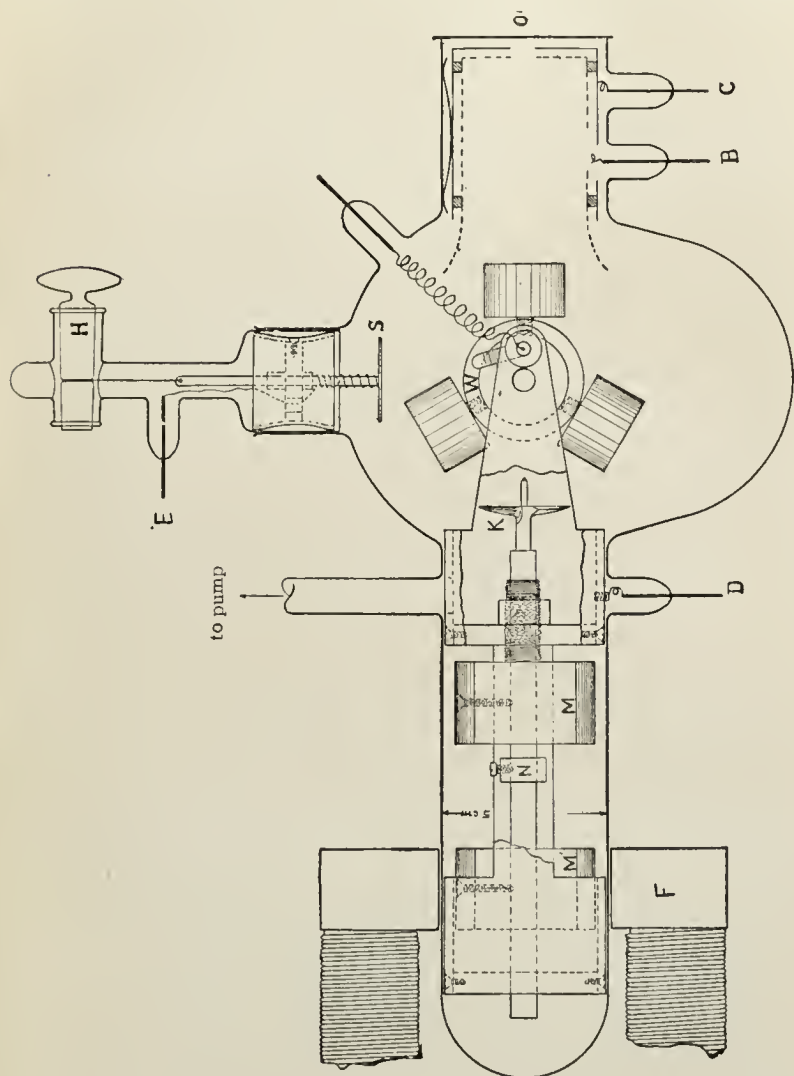


FIG. 33

charge to the quadrant electrometer which was attached to this gauze cylinder. For a complete test of the equation it was necessary also to measure the contact-



electromotive force between the new surface and a test plate  $S$ . This was done by another electromagnetic device shown in Fig. 32, but for further details the original paper may be consulted.<sup>1</sup> Suffice it here to say that Einstein's equation demands a linear relation between the applied positive volts and the frequency of the light, and it also demands that the slope of this line should be exactly equal to  $\left(\frac{h}{e}\right)$ . Hence from this slope, since  $e$  is known, it should be possible to obtain  $h$ . How perfect a linear relation is found may be seen from Fig. 34, which also shows that from the slope of this line  $h$  is found to be  $6.26 \times 10^{-27}$ , which is as close to the value obtained by Planck from the radiation laws as is to be expected from the accuracy with which the experiments in radiation can be made. The most reliable value of  $h$  obtained from a consideration of the whole of this work is

$$h = 6.56 \times 10^{-27}.$$

In the original paper will be found other tests of the Einstein equation, but the net result of all this work is to confirm in a very complete way the equation which Einstein first set up on the basis of his semi-corpuscular theory of radiant energy. And if this equation is of general validity it must certainly be regarded as one of the most fundamental and far-reaching of the equations of physics, and one which is destined to play in the future a scarcely less important rôle than Maxwell's equations have played in the past, for it must govern the transformation of all short-wave-length electromagnetic energy into heat energy.

<sup>1</sup> *Phys. Rev.*, VII (1916), 362.



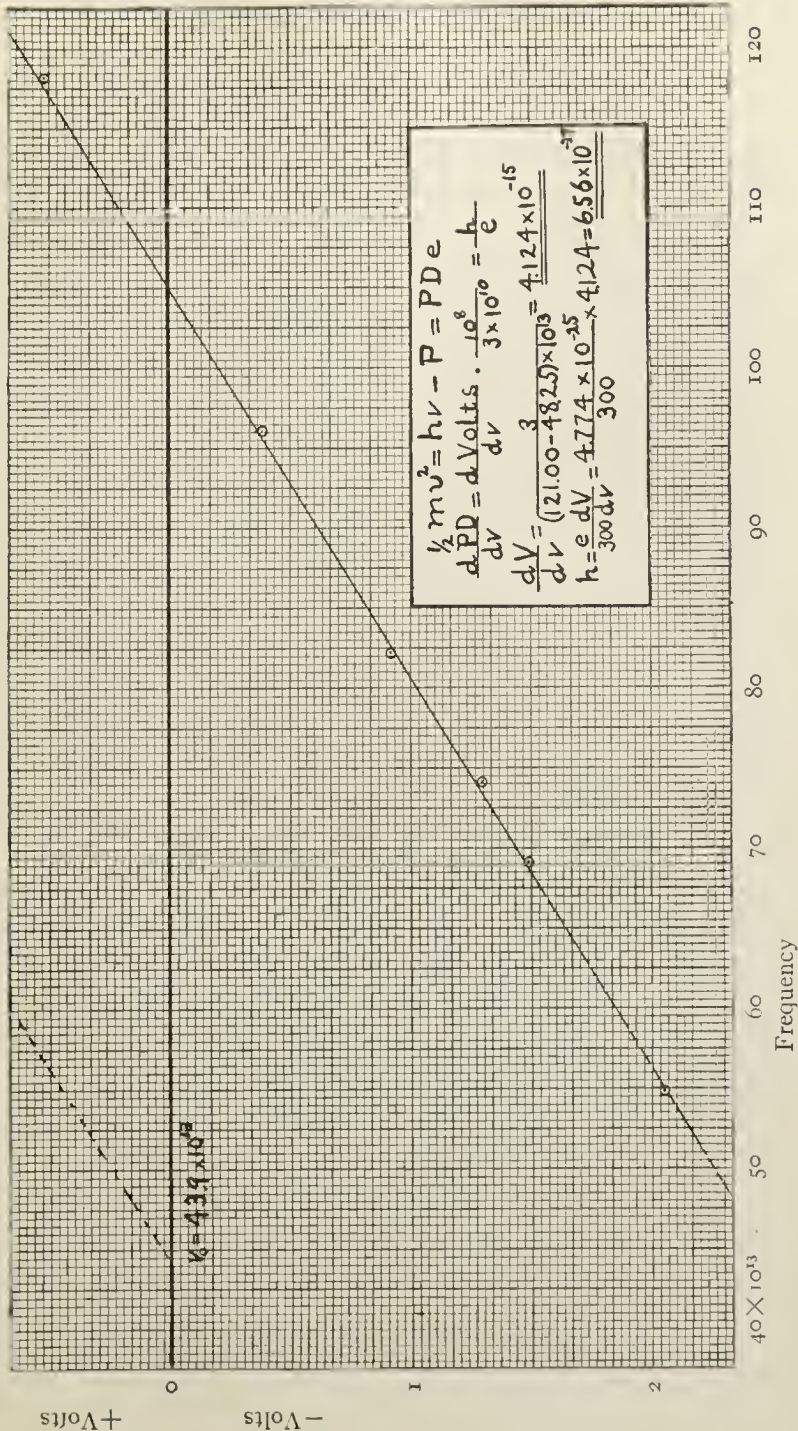


FIG. 34

## V. HISTORY OF EINSTEIN'S EQUATION

The whole of this chapter up to this point has been left practically as it was written for the first edition of this book in 1916. Now the altogether overwhelming proof that Einstein's equation is an exact equation of very general validity is perhaps the most conspicuous achievement of experimental physics during the past decade. Its history is briefly as follows.

As early as 1900 Planck<sup>1</sup> had been led from theoretical considerations to the conclusion that atoms radiated energy discontinuously in units which were equal to, or multiples of,  $h\nu$ , in which  $\nu$  is the natural frequency of the radiator, and  $h$  a universal constant which is now called Planck's  $h$ . He adopted the view that the seat of the discontinuity was *in the radiator*, not in the radiation after it had left the radiator, and in the second edition of his book modified the formulation of his theory so as to make this appear without any ambiguity.

It was in 1905, as stated above, that Einstein definitely put the discontinuity into the radiation itself, assuming that light itself consisted of darts of localized energy, "light-quantas," of amount  $h\nu$ . He further assumed that one of these light-quantas could transfer its energy undiminished to an electron, so that, in the photoelectric effect, the electron shot out from the metal with the energy  $h\nu - p$ , where  $p$  represents the work necessary to get it out of the metal.

In 1913 Bohr, in the development of his theory of spectra, without accepting Einstein's view as to the seat of the discontinuity, assumed an *equation* which was

<sup>1</sup> *Warme Strahlung*, 1st. ed.

precisely the inverse of Einstein's, i.e., he assumed that the energy lost when an electron jumps from one stationary state to another is wholly transformed into monochromatic radiation whose frequency is determined by equating the loss in energy  $E_1 - E_2$  to  $h\nu$ . In other words, *Einstein and Bohr together have set up a reciprocal and reversible relation between electronic and radiant energy.*

Up to 1914 no direct experimental proof had appeared for the correctness of this relation. In the photo-electric field discussion was active as to whether any definite maximum velocity of emission of electrons under the influence of monochromatic light existed, and although linear relations between energy and frequency had been reported by Ladenburg, Richardson and Compton, and Hughes, the range of frequencies available had been so small as to leave uncertainties in the minds of reviewers<sup>1</sup> and Planck's  $h$  had definitely as yet failed to appear.

The unambiguous experimental proofs of the correctness of the foregoing theoretical relation began with the publication of the accompanying photo-electric results<sup>2</sup> which were reported briefly in 1914, and submitted *in extenso* in September, 1915. These were in a form to prove the correctness of the Einstein equation; for monochromatic light of known frequency  $\nu$  fell upon a metal and the maximum energy of electronic ejection was found to be exactly determined by  $h\nu = \frac{1}{2}mv^2 - p$  as Einstein's equation required.

<sup>1</sup> Cf. R. Pohl u. P. Pringsheim, *Verh. der deutsch. phys. Ges.*, XV (1913), 637; Sommerfeld, *Atombau*, etc. (3d ed. 1922), p. 47; also *Phys. Rev.*, VII (1916), 18, 362.

<sup>2</sup> *Phys. Rev.*, IV (1914), 73; VI (1915), 55; and VII (1916), 362.

A year or two later Duane<sup>1</sup> and his associates had found unambiguous proof of the inverse effect. A target had been bombarded by electrons of known and constant energy ( $Ve = \frac{1}{2}mv^2$ ) and the maximum frequency of the emitted ether waves (general  $x$  radiation) was found to be precisely given by  $\frac{1}{2}mv^2 = h\nu$ .

D. L. Webster then proved that the characteristic X-ray frequencies of atoms begin to be excited at exactly the potential at which the energy of the stream of electrons which is bombarding the atoms has reached the value given by  $h\nu = \frac{1}{2}mv^2$  in which  $\nu$  is now the frequency of an absorption edge.<sup>2</sup> This checks Bohr's formulation of frequency-energy relations, since it shows that when an electron within an atom receives just enough energy by bombardment to be entirely removed from the atom, the total energy values of the frequencies emitted during its return are equal to the electronic energy of the original bombardment.

De Broglie<sup>3</sup> and Ellis,<sup>4</sup> on the other hand, have measured with great accuracy, by means of the deviability in a magnetic field, the velocities of electrons ejected from different sorts of atoms by monochromatic X-rays, and have completely confirmed by such photo-electric work in the X-ray field my previous results obtained with ultra-violet light. They here verify in great detail and with much elaboration the Einstein formulation

<sup>1</sup> *Phys. Rev.*, VI (1915), 166; *Proc. Nat. Acad.*, II (1916), 90; *Phys. Rev.*, VII (1916), 599; IX, 568; X (1917), 93 and 624.

<sup>2</sup> D. L. Webster and H. Clark, *Proc. Nat. Acad.*, III (1917), 18. Also Webster, *ibid.*, VI (1920), 26 and 639.

<sup>3</sup> Paper read before the Third Solvay Congress, 1921.

<sup>4</sup> *Proc. Roy. Soc.*, XCIX (1921), 261. See also the same, January, 1924.

$\frac{1}{2}mv^2 = h\nu - p$  where  $p$  now represents the work necessary to lift the electron out of any particular level in the atom.

Parallel to this very complete establishment of the validity in the X-ray field of the Einstein photoelectric equation, and of its inverse the Bohr equation, has come the rapid working out in the domain of optics of the very large field of ionizing and radiating potentials which has also involved the utilization and verification of the same reciprocal relation. This will be seen at once from the definition of the ionizing potential of an atom as the electronic energy which must be thrown into it by bombardment to just remove from it one of its outer electrons. Through the return of such removed electrons there is in general a whole spectral series emitted. Similarly the radiating potential of an atom is defined as the bombarding energy which must be supplied to it to just lift one of its outer electrons from its normal orbit to the first virtual orbit outside that normal orbit. When this electron drops back there is in general the emission of a single-line spectrum. All this work took its origin in the fundamental experiments of Franck and Hertz<sup>1</sup> on mercury vapor in 1914. From 1916-22 the field was worked out in great detail, especially in America by Foote and Mohler, Wood, McLennan, Davis and Goucher, and others.

Suffice it to say that whether the energy comes in the form of ether waves which through absorption in an atom lift an electron out of a normal orbit, so that the atom passes over to an excited or to an ionized state, or whether the energy enters in the form of a bombarding

<sup>1</sup> *Verh. der deutsch. phys. Ges.*, XV and XVI, 1914.



electron and reappears as a radiated frequency, *the reciprocal relation represented in the Einstein-Bohr equation  $E_1 - E_2 = h\nu$  has been found fulfilled in the most complete manner.*

In view of all these methods and experiments the general validity of the Einstein equation, first proved photo-electrically about ten years ago, is now universally conceded.

## VI. OBJECTIONS TO AN ETHER-STRING THEORY

In spite of the credentials which have just been presented for Einstein's equation, the essentially corpuscular theory out of which he got it has not yet met with general acceptance even by physicists of Bohr's type. There seems to be no possibility, at present, of bringing it into harmony with a whole group of well-established facts of physics.

The recent practically complete bridging of the gap between X-rays and light,<sup>1</sup> as well as that between heat waves and wireless waves,<sup>2</sup> with the perfectly continuous passage of the latter over into static electrical fields, appears to demand that, if we attempt to interpret high frequency electromagnetic waves—X-rays and light—in terms of undulatory “darts of light,” we also interpret wireless waves in the same way, and this in turn requires us to use a similar mechanism in the interpretation of static electrical fields. This brings us back to Thomson's ether-string theory, which seems to be a necessary part of Einstein's conception, if it is to have any physical basis whatever.

<sup>1</sup> Millikan and Bowen, *Phys. Rev.*, January, 1924.

<sup>2</sup> Nichols and Tear, *ibid.*, 1923.



Two very potent objections, however, may be urged against all forms of ether-string theory. The first is that no one has ever yet been able to show that such a theory can predict any one of the facts of interference. The second is that there is direct positive evidence against the view that the ether possesses a fibrous structure. For if a static electrical field has a fibrous structure, as postulated by any form of ether-string theory, "each unit of positive electricity being the origin and each unit of negative electricity the termination of a Faraday tube,"<sup>1</sup> then the force acting on one single electron between the plates of an air condenser cannot possibly vary *continuously* with the potential difference between the plates. Now in the oil-drop experiments<sup>2</sup> we actually study the behavior in such an electric field of one single, isolated electron and we find, over the widest limits, exact proportionality between the field strength and the force acting on the electron as measured by the velocity with which the oil drop to which it is attached is dragged through the air.

When we maintain the field constant and vary the charge on the drop, the granular structure of electricity is proved by the discontinuous changes in the velocity, but when we maintain the charge constant and vary the field the lack of discontinuous change in the velocity disproves the contention of a fibrous structure in the field, unless the assumption be made that there are an enormous number of ether strings ending in one electron. Such an assumption takes most of the virtue out of an ether-string theory.

<sup>1</sup> J. J. Thomson, *Electricity and Matter*, p. 9.

<sup>2</sup> *Phys. Rev.*, II (1913), 109.

Despite, then, the apparently complete success of the Einstein equation, the physical theory of which it was designed to be the symbolic expression is thus far so irreconcilable with a whole group of well-established facts that some of the most penetrating of modern physicists cannot as yet accept it, and we are somewhat in the position of having built a very perfect structure and then knocked out entirely the underpinning without causing the building to fall. It stands complete and apparently well tested, but without any visible means of support. These supports must obviously exist, and the most fascinating problem of modern physics is to find them. Experiment has outrun theory, or, better, guided by unacceptable theory, it has discovered relationships which seem to be of the greatest interest and importance, but the reasons for them are as yet not at all understood.

## VII. ATTEMPTS TOWARD A SOLUTION

It is possible, however, to go a certain distance toward a solution and to indicate some conditions which must be satisfied by the solution when it is found. For the energy  $h\nu$ , with which the electron is found by experiment to escape from the atom, must have come either from the energy stored up inside of the atom or else from the light. There is no third possibility. Now the fact that the energy of emission is the same, whether the body from which it is emitted is held within an inch of the source, where the light is very intense, or a mile away, where it is very weak, would seem to indicate that the light simply pulls a trigger in the atom which itself furnishes all the energy with which the electron escapes,

as was originally suggested by Lenard in 1902,<sup>1</sup> or else, if the light furnishes the energy, that light itself must consist of bundles of energy which keep together as they travel through space, as suggested in the Thomson-Einstein theory.

Yet the fact that the energy of emission is directly proportional to the frequency  $\nu$  of the incident light spoils Lenard's form of trigger theory, since, if the atom furnishes the energy, it ought to make no difference what kind of a wave-length pulls the trigger, while it ought to make a difference what kind of a gun, that is, what kind of an atom, is shot off. But both of these expectations are the exact opposite of the observed facts. *The energy of the escaping electron must come, then, in some way or other, from the incident light, or from other light of its frequency, since it is characteristic of that frequency alone.*

When, however, we attempt to compute on the basis of a spreading-wave theory how much energy an electron can receive from a given source of light, we find it difficult to find anything more than a very minute fraction of the amount which it actually acquires.

Thus, the total luminous energy falling per second from a standard candle on a square centimeter at a distance of 3 m. is 1 erg.<sup>2</sup> Hence the amount falling per second on a body of the size of an atom, i.e., of cross-section  $10^{-15}$  cm., is  $10^{-15}$  ergs, but the energy  $h\nu$  with which an electron is ejected by light of wave-length  $500\ \mu\mu$  (millionths millimeter) is  $4 \times 10^{-12}$  ergs, or four thousand times as much. Since not a third of the incident energy is in wave-lengths shorter than  $500\ \mu\mu$ , a

<sup>1</sup> *Ann. d. Phys.* (4), VIII (1902), 149.

<sup>2</sup> Drude, *Lehrbuch der Optik* (1906), p. 472.

surface of sodium or lithium which is sensitive up to  $500\ \mu\mu$  should require, even if all this energy were in one wave-length, which it is not, at least 12,000 seconds or 4 hours of illumination by a candle 3 m. away before any of its atoms could have received, all told, enough energy to discharge an electron. Yet the electron is observed to shoot out the instant the light is turned on. It is true that Lord Rayleigh has shown<sup>1</sup> that an atom may conceivably absorb wave-energy from a region of the order of magnitude of the square of a wave-length of the incident light rather than of the order of its own cross-section. This in no way weakens, however, the cogency of the type of argument just presented, for it is only necessary to apply the same sort of analysis to the case of  $\gamma$ -rays, the wave-length of which is sometimes as low as a hundredth of an atomic diameter ( $10^{-8}$  cm.), and the difficulty is found still more pronounced. Thus Rutherford<sup>2</sup> estimates that the total  $\gamma$ -ray energy radiated per second by one gram of radium cannot possibly be more than  $4.7 \times 10^4$  ergs. Hence at a distance of 100 meters, where the  $\gamma$ -rays from a gram of radium would be easily detectable, the total  $\gamma$ -ray energy falling per second on a square millimeter of surface, the area of which is ten-thousand billion times greater than that of an atom, would be  $4.7 \times 10^4 \div 4\pi \times 10^{10} = 4 \times 10^{-7}$  ergs. This is very close to the energy with which  $\beta$ -rays are actually observed to be ejected by these  $\gamma$ -rays, the velocity of ejection being about nine-tenths that of light. Although, then, it should take ten thousand billion seconds for the atom to gather in this much energy from

<sup>1</sup> *Phil. Mag.*, XXXII (1916), 188.

<sup>2</sup> *Radioactive Substances and Their Radiations*, p. 288.

the  $\gamma$ -rays, on the basis of classical theory, the  $\beta$ -ray is observed to be ejected with this energy as soon as the radium is put in place. This shows that if we are going to abandon the Thomson-Einstein hypothesis of localized energy, which is of course competent to satisfy these energy relations, there is no alternative but to assume that at some previous time the electron had absorbed and stored up from light of this wave-length enough energy so that it needed but a minute addition at the time of the experiment to be able to be ejected from the atom with the energy  $h\nu$ . What sort of an absorbing and energy-storing mechanism an atom might have which would give it the weird property of storing up energy to the value  $h\nu$ , where  $\nu$  is the frequency of the *incident* light, and then shooting it all out at once, is terribly difficult to conceive. Or, if the absorption is thought of as due to resonance it is equally difficult to see how there can be, in the atoms of a solid body, electrons having all kinds of natural frequencies so that some are always found to absorb and ultimately be ejected by impressed light of any particular frequency.

However, then, we may interpret the phenomenon of the emission of electrons under the influence of ether waves, whether upon the basis of the Thomson-Einstein assumption of bundles of localized energy traveling through the ether, or upon the basis of a peculiar property of the inside of an atom which enables it to absorb continuously incident energy and emit only explosively, *the observed characteristics of the effect seem to furnish proof that the emission of energy by an atom is a discontinuous or explosive process.* This was the fundamental assumption of Planck's so-called quantum theory

of radiation. The Thomson-Einstein theory makes both the absorption and the emission sudden or discontinuous, while the loading theory first suggested by Planck makes the absorption continuous and only the emission explosive.

The new facts in the field of radiation which have been discovered through the study of the properties of the electron seem, then, to require in any case a very fundamental revision or extension of classical theories of absorption and emission of radiant energy. The Thomson-Einstein theory throws the whole burden of accounting for the new facts upon the unknown nature of the ether, and makes radical assumptions about its structure. The loading theory leaves the ether alone and puts the burden of an explanation upon the unknown conditions and laws which exist inside the atom.

In the first edition of this book, finished in 1917, I expressed the view that the chances were in favor of the ultimate triumph of the second alternative. In 1921, however, I presented at the Third Solvay Congress some new photo-electric experiments<sup>1</sup> which seemed at the time to point strongly the other way.

These experiments consisted in showing with greater certainty than had been possible in earlier years<sup>2</sup> that the stopping potentials of different metals  $A$ ,  $B$ ,  $C$ , when brought in succession before the same Faraday cylinder  $F$  (see Fig. 35) and illuminated with a given frequency, were strictly identical. The significance of these results

<sup>1</sup> Millikan, *Phys. Rev.*, XVIII (1921), 236.

<sup>2</sup> Page, *Amer. Jour. Sci.*, XXXVI (1913), 501; Hennings and Kadesch, *Phys. Rev.*, VIII (1916), 217.



for the theory of quanta lay in the fact that I deduced from them the conclusion that in the photo-electric effect, contrary to preceding views including my own, the energy " $h\nu$ " is transferred without loss from the ether-waves to the free, i.e., the conduction electrons of the metal, and not merely to those bound in atoms. This seemed to take the absorbing mechanism out of the atom entirely, and to make the property of imparting the energy  $h\nu$  to an electron, whether free or bound, an intrinsic property of light itself.

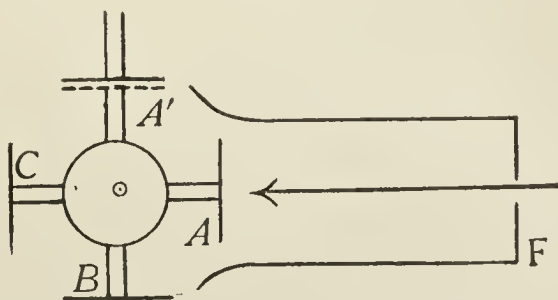


FIG. 35.—Showing how photo-electric stopping potentials of different metals are compared by rotating *B* and *C* in *vacuo* into the position of *A*.

But a beautiful discovery by Klein and Rosseland<sup>1</sup> a little later, in Bohr's Institute, made this conclusion unnecessary. For it showed that there was an intermediate process, namely, a so-called *collision of the second kind*, by means of which the energy  $h\nu$  might be transferred without loss, *indirectly* from the light-wave to the conduction electron, thus obviating the necessity of a *direct* transfer. In other words, the Klein and Rosseland discovery proved that the energy  $h\nu$  could be transferred from the light-wave to the conduction electron by being

<sup>1</sup> *Zeitschrift für Physik*, 4 (1921), 46.

absorbed first by an atom, which would thus be changed from the normal to the excited state, i.e., the state in which one of its electrons has been lifted from a normal to an outer orbit. This excited atom could then return to its normal state *without radiation* by a collision "of the second kind," which consists in transferring its whole absorbed energy  $h\nu$  to a free or conduction electron. The reality of this phenomenon has been experimentally checked by Franck and Cario.<sup>1</sup> This important discovery then left the evidence for localized light-quanta precisely where it was before.<sup>2</sup>

Within the past year, however, a young American physicist, Dr. A. H. Compton, of the University of Chicago, has discovered another new phenomenon which constitutes perhaps the best evidence yet found in favor of Einstein's hypothesis of localized light-quanta.

Compton's procedure is as follows. Assuming, for the sake of obtaining quantitative relations, the correctness of Einstein's hypothesis, he argues that when such a "light-quant" collides with a *free* electron the impact should be governed by the laws which hold for the collision between any material bodies. These are two in number, namely: (1) the principle of the conservation of energy; (2) the principle of the conservation of momentum (Newton's Third Law).

Now the energy of a light-quant, as heretofore shown, is  $h\nu$ . It moves with the speed of light,  $c$ , and if its momentum is taken as  $mc$ , it follows at once from the Einstein relativity relation between energy and mass,

<sup>1</sup> *Zeitschrift für Physik*, 10 (1922), 185.

<sup>2</sup> This was first called to my attention by Dr. Epstein, of the California Institute.

namely,  $\text{energy}/c^2 = m$ , that its momentum is  $\frac{h\nu}{c}$ . This is seen by substituting in the foregoing Einstein relation  $h\nu$  for energy. Or, if preferred, the same expression for momentum may be deduced easily from the established laws of light-pressure.

The qualitative results of the preceding assumptions are immediately seen to be as follows. The light-quant, by colliding with the free electron necessarily transfers some of its energy to it, and therefore, if it arrives with the energy  $h\nu_0$ , it must recoil from the impact at some angle  $\theta$  with a smaller energy  $h\nu_\theta$ , and therefore a lower frequency  $\nu_\theta$ , than that with which it impinged. In other words, *light waves should be changed from a higher frequency to a lower—from blue toward red—by impact with a free electron.*

A second qualitative result is that, since the mass of the light-quant, as defined above, is even for the hardest X-rays ( $\lambda = 0.1$  Angstrom), of the order of a tenth of the mass of the electron, it is impossible from the laws of elastic impact that it transfer more than a small part of its energy to it. In other words, *if Compton's assumptions are correct, the photo-electric effect, in which there certainly is such a complete transfer, cannot possibly represent the interaction between a light-wave and a free electron.* When the electron is *bound* in the atom there is no difficulty of this sort, for the huge mass of the atom then permits the momentum equation to be satisfied without forbidding the practically complete transfer of the energy to one of its electrons. From this point of view, then, the photo-electric effect represents the interaction between ether-waves and *bound* electrons—the Compton effect the interaction between ether-waves and *free* electrons.

The quantitative results which can be deduced from Compton's assumptions are definite and simple. Combining the energy and momentum equations in the manner shown in Appendix H he obtains easily the result

$$\Delta\lambda = .0484 \sin^2 \frac{1}{2}\theta,$$

in which  $\Delta\lambda$  represents the increase in wave-length due to the "scattering" of the incident beam by free electrons, and  $\theta$  is the angle between the original direction of the beam and the direction at which the scattered waves come to the measuring apparatus.

Compton then tested this relation experimentally,<sup>1</sup> using as his incident waves the characteristic X-rays from a molybdenum target, and as his scattering substance the free (or substantially free) electrons found in graphite. *He found indeed that the  $\alpha$ -line of molybdenum was shifted toward longer wave-lengths just as predicted, and in approximately the correct amount.* There was also an unshifted line presumably due to scattering by bound electrons.

Compton had used an ionization-chamber spectrometer for locating his lines. Ross<sup>2</sup> repeated these experiments at Stanford University, California, using the more accurate photographic plate for locating his lines, but still using graphite as the scattering substance. His published photograph shows a line shifted the correct amount and also an unshifted one, but he commented on the fact that the shifted line shows no sign of a separation of the  $\alpha_1$  and  $\alpha_2$  components while they are clearly separate in the direct picture.

<sup>1</sup> A. H. Compton, *Phys. Rev.*, XXI (1923), 483, 715; XXII (1923), 409.

<sup>2</sup> P. A. Ross, *Proc. Nat. Acad.*, VII (1923), 246.

Duane and his collaborators repeated the Compton experiments at Harvard, using again the ionization chamber method, and failed to obtain any trace of the Compton shift. At the February meeting of the Physical Society, 1924, they took the view that the Compton effect did not exist, but that what both Compton and Ross had observed was the  $\alpha$ -rays of molybdenum with their energy diminished by the work necessary to eject electrons from the K shell of the carbon atom.<sup>1</sup> This would actually produce a "scattered line" from carbon which would be practically coincident with Ross's published line, though it should not give a dependence of  $\Delta\lambda$  upon angle  $\theta$  such as Compton had observed.

A few weeks before the date of this writing, at the Norman Bridge Laboratory of Physics at Pasadena, Becker, Watson, and Smythe,<sup>2</sup> using aluminum as a scatterer, obtained a Compton-effect photograph which showed both components of the  $\alpha$ -rays of molybdenum displaced by an amount which could be measured with an accuracy of about 1 per cent (as checked by the author) and within this limit *the agreement with the displacement computed by the foregoing Compton equation was exact*. In this case the Duane-effect-line is completely removed from the Compton-effect-position, and it too was found upon the photographic plate. *This furnishes, I think, unambiguous evidence for the reality of the Compton effect*. Ross also informs me that he has obtained the Compton shifted line from a number of other elements besides carbon—elements in which the Duane effect could not possibly be confused with it.

<sup>1</sup> Duane and Clark, *ibid.*, February and March, 1924.

<sup>2</sup> Becker *et al.*, *Proc. Phys. Soc.*, April 26, 1924; *Phys. Rev.*, June, 1924.

The accompanying plate shows in Fig. 36 one of the Becker, Watson, and Smythe recent photographs. This one was not taken with sufficient resolution to show the  $\alpha$ -line as a doublet, but is more reproducible than the one that did. The direct images of both the  $\alpha$ - and  $\beta$ -lines of molybdenum are shown, labeled  $\alpha$  and  $\beta$ , and, a short distance to the right of each, appears the displaced Compton-shifted-line marked  $\alpha_c$  and  $\beta_c$ .

At the moment, then, Einstein's hypothesis of localized light-quanta is having new and remarkable successes. Duane,<sup>1</sup> Epstein,<sup>2</sup> and Ehrenfest<sup>3</sup> have perhaps made some slight advances also in the direction of accounting for interference in terms of it. But the theory is as yet woefully incomplete and hazy. About all that we can say now is that we seem to be driven by newly discovered relations in the field of radiation to the hypothetical use of a fascinating conception which we cannot as yet reconcile at all with well-established wave-phenomena.

To be living in a period which faces such a complete reconstruction of our notions as to the way in which ether waves are absorbed and emitted by matter is an inspiring prospect. The atomic and electronic worlds have revealed themselves with beautiful definiteness and wonderful consistency to the eye of the modern physicist, but their relation to the world of ether waves is still to him a profound mystery for which the coming generation has the incomparable opportunity of finding a solution.

In conclusion there is given a summary of the most important physical constants the values of which it has

<sup>1</sup> *Proc. Nat. Acad. Sci.*, IX, (1923), 158; Compton, *ibid.*, p. 359.

<sup>2</sup> *Ibid.*, 1924.

<sup>3</sup> *Ibid.*





$\beta$   $\beta_c$   $\alpha$   $\alpha_c$

FIG. 36.—THE COMPTON EFFECT

The photograph shows the change of wave-length of ether-waves, from blue toward red, because of scattering by free electrons.  $\alpha$  and  $\beta$  are the initial characteristic X-ray lines of molybdenum,  $\alpha_c$  and  $\beta_c$  these same lines after suffering scattering in aluminum.



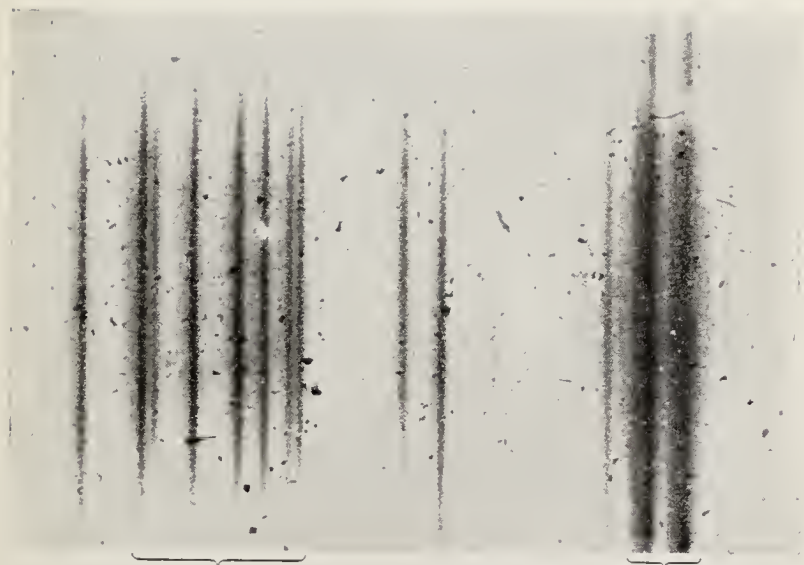


FIG. 37.—FINE STRUCTURE OF SPECTRAL LINES IN THE EXTREME  
ULTRA-VIOLET

The photograph shows the character of the resolution obtained in the recent study by Bowen and Millikan of the fine structure of spectral lines in the extreme ultra-violet. The seven lines in brackets on the left are components of the  $834.0$  oxygen line. Their total separation is but about two angstroms. The bracketed doublet on the right is one of the many studied, the separation of which is predicted by the theoretical-relativity-doublet formula.



become possible to fix,<sup>1</sup> within about the limits indicated, through the isolation and measurement of the electron.

The electron.....  $e = (4.774 \pm 0.005) \times 10^{-10}$

The Avogadro constant.....  $N = (6.062 \pm 0.006) \times 10^{23}$

Number of gas molecules per cc. at

0° C. 76 cm.....  $n = (2.705 \pm 0.003) \times 10^{19}$

Kinetic energy of translation of a

molecule at 0° C.....  $E_0 = (5.621 \pm 0.006) \times 10^{-14}$

Change of translational molecular

energy per ° C.....  $\epsilon = (2.058) \pm 0.002 \times 10^{-16}$

Mass of an atom of hydrogen in grams  $m = (1.662 \pm 0.002) \times 10^{-24}$

Planck's element of action.....  $h = (6.547 \pm 0.013) \times 10^{-27}$

Wien constant of spectral radiation  $C_2 = 1.4312 \pm 0.0030$

Stefan-Boltzmann constant of total

radiation.....  $\sigma = (5.72 \pm 0.034) \times 10^{-12}$

Grating spacing in calcite.....  $d = 3.029 \pm 0.001 \text{ \AA}$

<sup>1</sup> See *Proc. Nat. Acad. Sci.*, III (1917), 236; also *Phil. Mag.*, July, 1917.

## APPENDIX A

### FROM MOBILITIES AND DIFFUSION COEFFICIENTS

If we assume that gaseous ions, which are merely charged molecules or clusters of molecules, act exactly like the uncharged molecules about them, they will tend to diffuse just as other molecules do and will exert

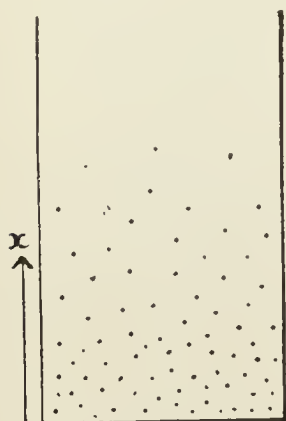


FIG. 38

a partial gas pressure of exactly the same amount as would an equal number of molecules of any gas. Imagine then the lower part of the vessel of Fig. 38 to be filled with gas through which ions are distributed and imagine that these ions are slowly diffusing upward. Let  $n'$  be the ionic concentration, i.e., the number of ions per cubic centimeter at any distance  $x$  from the bottom of the vessel. Then the number  $N$  of ions which pass

per second through 1 sq. cm. taken perpendicular to  $x$  at a distance  $x$  from the bottom must be directly proportional to the concentration gradient  $\frac{dn'}{dx}$  and the factor of proportionality in a given gas is by definition the diffusion coefficient  $D$  of the ions through this gas, i.e.,

$$N = D \frac{dn'}{dx} \dots\dots\dots (42)$$

But since  $N$  is also equal to the product of the average velocity  $V$  with which the ions are streaming upward at



$x$  by the number of ions per cubic centimeter at  $x$ , i.e., since  $N \doteq n'V$ , we have from equation (42)

$$V = \frac{D}{n'} \frac{dn'}{dx}.$$

The force which is acting on these  $n'$ -ions to cause this upward motion is the difference in the partial pressure of the ions at the top and bottom of a centimeter cube at the point  $x$ . It is, therefore, equal to  $\frac{dp}{dx}$  dynes, and the ratio between the force acting and the velocity produced by it is

$$\frac{\frac{dp}{dx}}{\frac{D}{n'} \frac{dn'}{dx}}.$$

Now this ratio must be independent of the particular type of force which is causing the motion. Imagine then the same  $n'$ -ions set in motion, not by the process of diffusion, but by an electric field of strength  $F$ . The total force acting on the  $n'$ -ions would then be  $Fen'$ , and if we take  $v$  as the velocity produced, then the ratio between the force acting and the velocity produced will now be  $\frac{Fen'}{v}$ . By virtue then of the fact that this ratio is constant, whatever kind of force it be which is causing the motion, we have

$$\frac{Fen'}{v} = \frac{\frac{dp}{dx}}{\frac{D}{n'} \frac{dn'}{dx}} \dots\dots\dots (43)$$

Now if  $v_0$  denote the velocity in unit field, a quantity which is technically called the "ionic mobility,"  $\frac{v}{F} = v_0$ . Again since the partial pressure  $p$  is proportional to  $n'$ , i.e., since  $p = Kn'$ , it follows that  $\frac{dp}{p} = \frac{dn'}{n'}$ . Hence equation (43) reduces to

$$\frac{en'}{v_0} = \frac{1}{D \frac{p}{p}}$$

or

$$v_0 = De \frac{n'}{p} \dots \dots \dots (44)$$

But if we assume that, so far as all pressure relations are concerned, the ions act like uncharged molecules (this was perhaps an uncertain assumption at the time, though it has since been shown to be correct), we have  $\frac{n'}{p} = \frac{n}{P}$  in which  $n$  is the number of molecules per cubic centimeter in the air and  $P$  is the pressure produced by them, i.e.,  $P$  is atmospheric pressure. We have then from equation (44)

$$ne = \frac{v_0 P}{D} \dots \dots \dots (45)$$

## APPENDIX B

### TOWNSEND'S FIRST ATTEMPT AT A DETERMINATION OF $e$

Fig. 39' shows the arrangement of apparatus used. The oxygen rising from the electrode  $E$  is first bubbled through potassium iodide in  $A$  to remove ozone, then through water in  $B$  to enable the ions to form a cloud. This cloud-laden air then passes through a channel in an electrical insulator—a paraffin block  $P$ —into the tubes

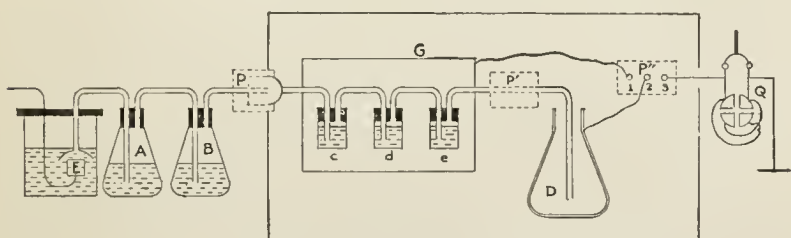


FIG. 39

$c, d, e$ , which contain concentrated sulphuric acid. These drying tubes remove all the moisture from the air and also such part of the charge as is held on ions which in the process of bubbling through  $c, d, e$  have actually touched the sulphuric acid. The dry air containing the rest of the charge passes out through a channel in the paraffin block  $P'$  into the flask  $D$ . (If the gas being studied was lighter than air, e.g., hydrogen,  $D$  was of course inverted.) The outside of  $D$  is covered with tin foil which is connected to one of the three mercury cups held by the paraffin block  $P''$ . If the air in  $D$  contained

at first no charge, then an electrical charge exactly equal to the quantity of electricity which enters the flask  $D$  will appear by induction on the tin-foil coating which covers this flask and this quantity  $q_1$  can be measured by connecting the mercury cup 2 to cup 3 which is connected to the quadrant electrometer  $Q$ , and observing the deflection per minute. Precisely similarly the total quantity of electricity which is left per minute in the drying tubes  $c, d, e$  is exactly equal to the quantity which appears by induction on the outer walls of the hollow metal vessel  $G$ , which surrounds the tubes  $c, d, e$ . This quantity  $q_2$  can be measured by connecting mercury cup 1 to cup 3 and observing the deflection per minute of the quadrant electrometer. The number of cubic centimeters of gas which pass through the apparatus per minute is easily found from the number of amperes of current which are used in the electrolysis apparatus  $E$  and the electrochemical equivalent of the gas. By dividing the quantities of electricity appearing per minute in  $D$  and  $G$  by the number of cubic centimeters of gas generated per minute we obtain the total charge per cubic centimeter carried by the cloud.

The increase in weight of the drying tubes  $c, d, e$  per cubic centimeter of gas passing, minus the weight per cubic centimeter of saturated water vapor, gives the weight of the cloud per cubic centimeter. This completes the measurements involved in (2) and (3), p. 47.

As to (4), p. 48, the average size of the droplets of water Townsend found by passing the cloud emerging from  $B$  into a flask and observing how long it took for the top of the cloud to settle a measured number of centimeters. The radius of the drops could then be

obtained from a purely theoretical investigation made by Sir George Stokes,<sup>1</sup> according to which the velocity  $v_1$  of fall of a spherical droplet through a gas whose coefficient of viscosity was  $\eta$  is given by

$$v_1 = \frac{2}{9} \frac{ga^2}{\eta} \sigma$$

in which  $\sigma$  is the density of the droplet. From this Townsend got the average radius  $a$  of the droplets and computed their average weight  $m$  by the familiar formula  $m = \frac{4}{3} \pi a^3 \sigma$ . He was then ready to proceed as in (5), see p. 48.

<sup>1</sup> Lamb, *Hydrodynamics*, 1895, p. 533.

## APPENDIX C

### THE BROWNIAN-MOVEMENT EQUATION

A very simple derivation of this equation of Einstein has been given by Langevin of Paris<sup>1</sup> essentially as follows: From the kinetic theory of gases we have  $PV = RT = \frac{1}{3}N\overline{mc^2}$  in which  $\overline{c^2}$  is the average of the squares of the velocities of the molecules,  $N$  the number of molecules in a gram molecule, and  $m$  the mass of each. Hence the *mean* kinetic energy of agitation  $E$  of each molecule is given by  $E = \frac{1}{2}m\overline{c^2} = \frac{3}{2} \frac{RT}{N}$ .

Since in observations on Brownian movements we record only motions along one axis, we shall divide the total energy of agitation into three parts, each part corresponding to motion along one of the three axes, and, placing the velocity along the  $x$ -axis equal to  $\frac{dx}{dt}$ , we have

$$\frac{E}{3} = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2} \frac{RT}{N} \dots\dots\dots (46)$$

Every Brownian particle is then moving about, according to Einstein's assumption, with a mean energy of motion along each axis equal to  $\frac{1}{2} \frac{RT}{N}$ . This motion is due to molecular bombardment, and in order to write an equation for the motion at any instant of a particle subjected to such forces we need only to know (1) the

<sup>1</sup> *Comptes Rendus*, CXLVI (1908), 530.



value  $X$  of the  $x$ -component of all the blows struck by the molecules at that instant, and (2) the resistance offered by the medium to the motion of the particle through it. This last quantity we have set equal to  $Kv$  and have found that in the case of the motion of oil droplets through a gas  $K$  has the value  $6\pi\eta a \left(1 + A \frac{l}{a}\right)^{-1}$ .

We may then write the equation of motion of the particle at any instant under molecular bombardment in the form

$$m \frac{d^2x}{dt^2} = -K \frac{dx}{dt} + X \dots\dots\dots (47)$$

Since in the Brownian movements we are interested only in the absolute values of displacements without regard to their sign, it is desirable to change the form of this equation so as to involve  $x^2$  and  $\left(\frac{dx}{dt}\right)^2$ . This can be done by multiplying through by  $x$ . We thus obtain, after substituting for  $x \frac{d^2x}{dt^2}$  its value  $\frac{1}{2} \frac{d^2(x^2)}{dt^2} - \left(\frac{dx}{dt}\right)^2$ ,

$$\frac{m}{2} \frac{d^2(x^2)}{dt^2} - m \left(\frac{dx}{dt}\right)^2 = -\frac{K}{2} \frac{d(x^2)}{dt} + Xx \dots\dots\dots (48)$$

Langevin now considers the *mean* result arising from applying this equation at a given instant to a large number of different particles all just alike.

Writing then  $\bar{\varepsilon}$  for  $\frac{d(\overline{x^2})}{dt}$  in which  $\overline{x^2}$  denotes the mean of all the large number of different values of  $x^2$ , he gets after substituting  $\frac{RT}{N}$  for  $m \left(\frac{dx}{dt}\right)^2$ , and remembering that

in taking the mean, since the  $X$  in the last term is as likely to be positive as negative and hence that  $\overline{Xx}=0$ ,

$$\frac{m}{2} \frac{dz}{dt} - \frac{RT}{N} = -\frac{Kz}{2}.$$

Separating the variables this becomes

$$\frac{dz}{\left(z - \frac{2RT}{NK}\right)} = -\frac{K}{m} dt,$$

which yields upon integration between the limits 0 and  $\tau$

$$z = \frac{2RT}{NK} + Ce^{-\frac{K}{m}\tau} \dots\dots\dots (49)$$

For any interval of time  $\tau$  long enough to measure this takes the value of the first term. For when Brownian movements are at all observable,  $a$  is  $10^{-4}$  cm. or less, and since  $K$  is roughly equal to  $6\pi\eta a$  we see that, taking the density of the particle equal to unity,

$$\frac{m}{K} = \frac{\frac{4}{3}\pi(10^{-4})^3}{6\pi \cdot 00018 \times 10^{-4}} = 10^{-5}.$$

Hence when  $\tau$  is taken greater than about  $10^{-5}$  seconds,  $e^{-\frac{K}{m}\tau}$  rapidly approaches zero, so that for any measurable time intervals

$$z = \frac{2RT}{NK}$$

or

$$\frac{d(\overline{x^2})}{dt} = \frac{2RT}{NK}$$

and, letting  $\overline{\Delta x^2}$  represent the change in  $\overline{x^2}$  in the time  $\tau$

$$\overline{\Delta x^2} = \frac{2RT}{NK} \tau \dots\dots\dots (50)$$

This equation means that if we could observe a large number  $n$  of exactly similar particles through a time  $\tau$ , square the displacement which each undergoes along the  $x$ -axis in that time, and average all these squared displacements, we should get the quantity  $\frac{2RT}{NK} \tau$ . But we must obviously obtain the same result if we observe the same identical particle through  $n$ -intervals each of length  $\tau$  and average these  $n$ -displacements. The latter procedure is evidently the more reliable, since the former must assume the exact identity of the particles.

## APPENDIX D

### THE INERTIA OR MASS OF AN ELECTRICAL CHARGE ON A SPHERE OF RADIUS $a$

If Fig. 40 represents a magnet of pole area  $A$ , whose two poles are  $d$  cm. apart, and have a total magnetization  $M$ , a density of magnetization  $\sigma$ , and a field strength between them of  $H$ , then the work necessary to carry a unit pole from  $M$  to  $M'$  is  $Hd$ , and the work necessary to create the poles  $M$  and  $M'$ , i.e., to carry  $M$  units of magnetism across again against a mean field strength  $\frac{H}{2}$  is  $\frac{HMd}{2}$ . Hence the total energy  $E_1$  of the magnetic field is given by

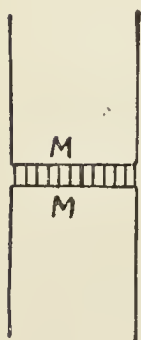


FIG. 40

$$E_1 = \frac{HMd}{2} = \frac{HA\sigma d}{2},$$

but since  $H = 4\pi\sigma$

$$E_1 = \frac{H^2 Ad}{8\pi},$$

or since  $Ad$  is the volume of the field the energy  $E$  per unit volume of the magnetic field is given by

$$E = \frac{H^2}{8\pi} \dots \dots \dots (51)$$

Now the strength of the magnetic field at a distance  $r$  from a moving charge in the plane of the charge is  $\frac{ev}{r^2}$ , if  $e$  is the charge and  $v$  its speed. Also the magnetic field strength at a point distant  $r\theta$  from the charge,  $\theta$  being

the angle between  $r$  and the direction of motion, is given by

$$H = \frac{ev}{r^2} \sin \theta.$$

Hence the total energy of the magnetic field created by the moving charge is

$$\int E d\tau = \int \frac{H^2}{8\pi} d\tau$$

in which  $\tau$  is an element of volume and the integration is extended over all space. But in terms of  $v$ ,  $\theta$ , and  $\phi$ .

$$d\tau = r d\theta, dr, r \sin \theta d\phi$$

$\therefore$  Total energy =

$$\frac{e^2 v^2}{8\pi} \int \frac{\sin^2 \theta}{r^4} d\tau = \frac{e^2 v^2}{8\pi} \int_a^\infty \frac{dr}{r^2} \int_0^{2\pi} d\phi \int_0^\pi \sin^3 \theta d\theta = \frac{e^2 v^2}{3a}.$$

Since kinetic energy  $= \frac{1}{2} m v^2$ , the mass-equivalent  $m$  of the moving charge is given by setting

$$\begin{aligned} \frac{1}{2} m v^2 &= \frac{e^2 v^2}{3a} \\ \therefore m &= \frac{2}{3} \frac{e^2}{a} \dots\dots\dots (52) \end{aligned}$$

The radius of the spherical charge which would have a mass equal to the observed mass of the negative electron is found by inserting in the last equation  $e = 4.774 \times 10^{-10}$

electrostatic units =  $1.591 \times 10^{-20}$  electromagnetic units  
 and  $\frac{e}{m} = 1.767 \times 10^7$  electromagnetic units. This gives  
 $a = 1.9 \times 10^{-13}$  cm.

The expression just obtained for  $m$  obviously holds only so long as the magnetic field is symmetrically distributed about the moving charge, as assumed in the integration, that is, so long as  $v$  is small compared with the velocity of light. When  $v$  exceeds .1 the speed of light  $c$ , the mass of the charge begins to increase measurably and becomes infinite at the speed of light. According to the theory developed by Lorentz, if the mass for slow speeds is called  $m_0$  and the mass at any speed  $v$  is called  $m$ , then

$$\frac{m}{m_0} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \dots \dots \dots (53)$$

This was the formula which Bucherer found to hold accurately for the masses of negative electrons whose speeds ranged from .3 to .8 that of light.



## APPENDIX E

### MOLECULAR CROSS-SECTION AND MEAN FREE PATH

If there is one single molecule at rest in a cubical space 1 cm. on a side, the chance that another molecule which is shot through the cube will impinge upon the one contained is clearly  $\frac{\pi d^2}{1}$  in which  $d$  is the mean diameter of the two molecules. If there are  $n$  contained molecules the chance is multiplied by  $n$ , that is, it becomes  $\frac{n\pi d^2}{1}$ . But on the average the chance of an impact in going a centimeter is the number of impacts actually made in traversing this distance. The mean free path  $l$  is the distance traversed divided by the number of impacts made in going that distance. Hence

$$l = \frac{1}{n\pi d^2} \dots\dots\dots (54)$$

This would be the correct expression for the mean free path of a molecule which is moving through a group of molecules at rest. If, however, the molecules are all in motion they will sometimes move into a collision which would otherwise be avoided, so that the collisions will be more numerous when the molecules are in motion than when at rest—how much more numerous will depend upon the law of distribution of the speeds of the molecules. It is through a consideration of the Maxwell

distribution law that the factor  $\sqrt{2}$  is introduced into the denominator (see Jeans, *Dynamical Theory of Gases*) so that equation (54) becomes

$$l = \frac{1}{\sqrt{2}n\pi d^2} \dots\dots\dots (55)$$

## APPENDIX F

### NUMBER OF FREE POSITIVE ELECTRONS IN THE NUCLEUS OF AN ATOM BY RUTHERFORD'S METHOD

If  $N$  represents the number of free positive electrons in the nucleus,  $e$  the electronic charge,  $E$  the known charge on the  $\alpha$ -particle, namely  $2e$ , and  $\frac{1}{2}mV^2$  the known kinetic energy of the  $\alpha$ -particle, then, since the inertias of the negative electrons are quite negligible in comparison with that of the  $\alpha$ -particle, if the latter suffers an appreciable change in direction in passing through an atom it will be due to the action of the nuclear charge. If  $b$  represents the closest possible approach of the  $\alpha$ -particle to the center of the nucleus, namely, that occurring when the collision is "head on," and the  $\alpha$ -particle is thrown straight back upon its course, then the original kinetic energy  $\frac{1}{2}mV^2$  must equal the work done against the electric field in approaching to the distance  $b$ , i.e.,

$$\frac{1}{2}mV^2 = \frac{N e E}{b} \dots\dots\dots (56)$$

Suppose, however, that the collision is not "head on," but that the original direction of the  $\alpha$ -particle is such that, if its direction were maintained, its nearest distance of approach to the nucleus would be  $p$  (Fig. 41). The deflection of the  $\alpha$ -particle will now be, not  $180^\circ$ , as before, but some other angle  $\phi$ . It follows simply from

the geometrical properties of the hyperbola and the elementary principles of mechanics that

$$p = \frac{b}{2} \cot \frac{\phi}{2} \dots\dots\dots (57)$$

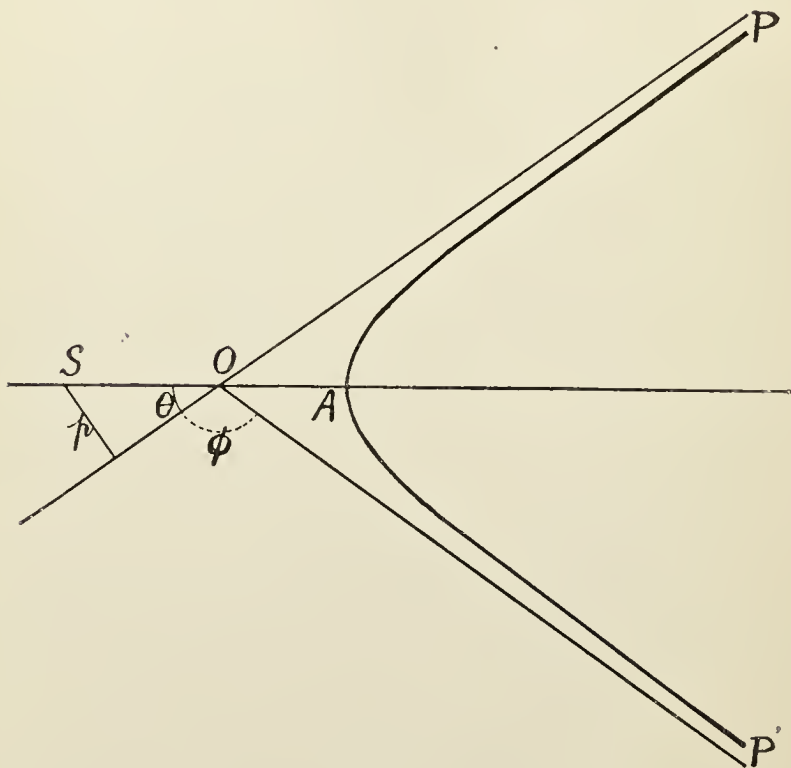


FIG. 41

For let  $PAP'$  represent the path of the particle and let  $POA = \theta$ . Also let  $V$  = velocity of the particle on entering the atom and  $v$  its velocity at  $A$ . Then from the conservation of angular momentum

$$pV = SA \cdot v \dots\dots\dots (58)$$

and from conservation of energy

$$\frac{1}{2}mV^2 = \frac{1}{2}mv^2 + \frac{NeE}{SA}$$

$$\therefore v^2 = V^2 \left( 1 - \frac{b}{SA} \right) \dots\dots\dots (59)$$

Since the eccentricity  $\epsilon = \sec \theta$ , and for any conic the focal distance is the eccentricity times one-half the major axis, i.e.,  $SO = OA \cdot \epsilon$ , it follows that

$$SA = SO + OA = SO \left( 1 + \frac{1}{\epsilon} \right) = p \csc \theta (1 + \cos \theta) = p \cot \frac{\theta}{2}.$$

But from equations (58) and (59)

$$p^2 = SA(SA - b) = p \cot \frac{\theta}{2} \left( p \cot \frac{\theta}{2} - b \right)$$

$$\therefore b = 2p \cot \theta \dots\dots\dots (60)$$

and since the angle of deviation  $\phi$  is  $\pi - 2\theta$ , it follows that

$$\cot \frac{\phi}{2} = \frac{2p}{b} \dots\dots\dots (61) \quad \text{Q.E.D.}$$

Now it is evident from the method used in Appendix E that if there are  $n$  atoms per cubic centimeter of a metal foil of thickness  $t$ , and if each atom has a radius  $R$ , then the probability  $M$  that a particle of size small in comparison with  $R$  will pass through one of these atoms in shooting through the foil is given by

$$M = \pi R^2 nt.$$

Similarly the probability  $m$  that it will pass within a distance  $p$  of the center of an atom is

$$m = \pi p^2 n t.$$

If this probability is small in comparison with unity, it represents the fraction  $\rho$  of any given number of particles shooting through the foil which will actually come within a distance  $p$  of the nucleus of an atom of the foil.

The fraction of the total number which will strike within radii  $p$  and  $p+dp$  is given by differentiation as

$$dm = 2\pi p n t \cdot dp$$

but from equation (57)

$$dp = -\frac{b}{2} c \sec^2 \frac{\phi}{2} d\phi$$

$$\therefore dm = -\frac{\pi}{4} n t b^2 \cot \frac{\phi}{2} \sec^2 \frac{\phi}{2} d\phi.$$

Therefore the fraction  $\rho$  which is deflected between the angles  $\phi_1$  and  $\phi_2$  is given by integration as

$$\rho = \frac{\pi}{4} n t b^2 \left( \cot^2 \frac{\phi_1}{2} - \cot^2 \frac{\phi_2}{2} \right)$$

It was this fraction of a given number of  $\alpha$ -particles shot into the foil which Geiger and Marsden found by direct count by the scintillation method to be deflected through the angles included between any assigned limits  $\phi_1$  and  $\phi_2$ . Since  $n$  and  $t$  are known,  $b$  could be at once obtained. It was found to vary with the nature of the



atom, being larger for the heavy atoms than for the lighter ones, and having a value for gold of  $3.4 \times 10^{-12}$  cm. This is then an upper limit for the size of the nucleus of the gold atom.

As soon as  $b$  has thus been found for any atom, equation (56) can be solved for  $N$ , since  $E$ ,  $e$ , and  $\frac{1}{2}m\bar{v}^2$  are all known. It is thus that the number of free positive electrons in the nucleus is found to be roughly half the atomic weight of the atom, and that the size of the nucleus is found to be very minute in comparison with the size of the atom.

## APPENDIX G

### BOHR'S THEORETICAL DERIVATION OF THE VALUE OF THE RYDBERG CONSTANT

The Newtonian equation of a circular orbit of an electron  $e$  rotating about a central attracting charge  $E$ , at a distance  $a$ , with a rotational frequency  $n$ , is

$$\frac{eE}{a^2} = (2\pi n)^2 ma \dots\dots\dots (62)$$

The kinetic energy of the electron is  $\frac{1}{2}m(2\pi na)^2 = \frac{1}{2}\frac{eE}{a}$ .

The work required to move the electron from its orbit to a position at rest at infinity is  $\frac{eE}{a} - \frac{1}{2}m(2\pi na)^2 = \frac{1}{2}\frac{eE}{a}$ .

If we denote this quantity of energy by  $T$ , it is seen at once that

$$\left. \begin{aligned} 2a &= \frac{eE}{T} \\ n &= \frac{\sqrt{2}T^{\frac{3}{2}}}{\pi eE\sqrt{m}} \dots\dots\dots \end{aligned} \right\} \dots\dots\dots (63)$$

If we combine this with (37), p. 213, there results at once

$$T = \frac{2\pi^2 me^2 E^2}{\tau^2 h^2} \quad 2a = \frac{\tau^2 h^2}{2\pi^2 meE} \quad n = \frac{4\pi^2 me^2 E^2}{\tau^3 h^3} \dots\dots (64)$$

Upon change in orbit the radiated energy must be

$$T_{\tau_1} - T_{\tau_2} = \frac{2\pi^2 me^2 E^2}{h^2} \left( \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right),$$

and, if we place this equal to  $h\nu$ , there results the Balmer formula (34), p. 210,

$$\nu = N \left( \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right)$$

in which

$$N = \frac{2\pi^2 e^2 E^2}{h^3}.$$

Since for hydrogen  $E=e$ , we have

$$N = \frac{2\pi^2 m e^4}{h^3}$$

and from (60)

$$a = \frac{\tau^2 h^3}{4\pi^2 m e^4}.$$

## APPENDIX H

### A. H. COMPTON'S THEORETICAL DERIVATION OF THE CHANGE IN THE WAVE-LENGTH OF ETHER-WAVES BECAUSE OF SCATTERING BY FREE ELECTRONS

Imagine, as in Fig. 42*A*, that an X-ray quantum of frequency  $\nu_0$  is scattered by an electron of mass  $m$ . The momentum of the incident ray will be  $h\nu_0/c$ , where  $c$  is the velocity of light and  $h$  is Planck's constant, and that

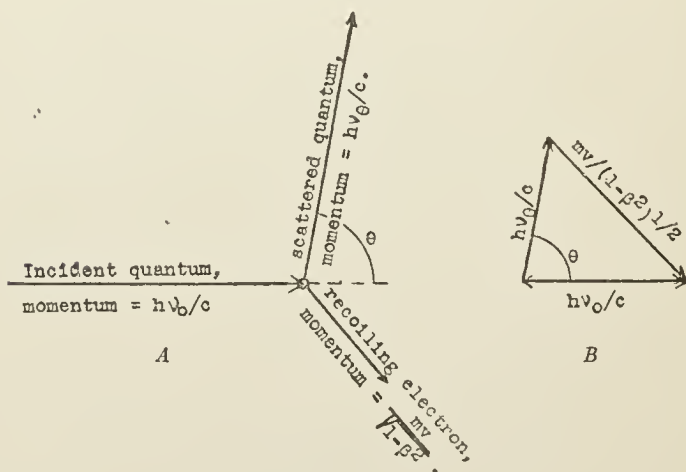


FIG. 42

of the scattered ray is  $h\nu_\theta/c$  at an angle  $\theta$  with the initial momentum. The principle of the conservation of momentum accordingly demands that the momentum of recoil of the scattering electron shall equal the vector difference between the momenta of these two rays, as in

Fig. 42*B*. The momentum of the electron,  $m\beta c/\sqrt{1-\beta^2}$ , is thus given by the relation

$$\left(\frac{m\beta c}{\sqrt{1-\beta^2}}\right)^2 = \left(\frac{h\nu_0}{c}\right)^2 + \left(\frac{h\nu_\theta}{c}\right)^2 - 2\frac{h\nu_0}{c} \cdot \frac{h\nu_\theta}{c} \cos \theta, \dots (65)$$

where  $\beta$  is the ratio of the velocity of recoil of the electron to the velocity of light. But the energy  $h\nu_\theta$  in the scattered quantum is equal to that of the incident quantum  $h\nu_0$  less the kinetic energy of recoil of the scattering electron, i.e.,

$$h\nu_\theta = h\nu_0 - mc^2 \left( \frac{1}{\sqrt{1-\beta^2}} - 1 \right) \dots \dots \dots (66)$$

We thus have two independent equations containing the two unknown quantities  $\beta$  and  $\nu_\theta$ . On solving the equations we find

$$\nu_\theta = \nu_0 / (1 + 2\alpha \sin^2 \frac{1}{2}\theta), \dots \dots \dots (67)$$

where

$$\alpha = h\nu_0 / mc^2 = h / mc\lambda_0 \dots \dots \dots (68)$$

or, in terms of wave-length instead of frequency,

$$\lambda_\theta = \lambda_0 + (2h/mc) \sin^2 \frac{1}{2}\theta \dots \dots \dots (69)$$

Substituting the accepted values of  $h$ ,  $m$ , and  $c$ ,

$$\lambda_\theta - \lambda_0 = \Delta\lambda = 0.0484 \sin^2 \frac{1}{2}\theta \dots \dots \dots (70)$$

# APPENDIX I

## THE ELEMENTS, THEIR ATOMIC NUMBERS, ATOMIC WEIGHTS, AND CHEMICAL POSITIONS

1 H  
1.008

I	II	III	IV	V	VI	VII	VIII
2 He 3.99	3 Li 6.94	4 Be 9.1	5 B 11.0	6 C 12.00	7 N 14.01	8 O 16.00	9 F 19.0
10 Ne 20.2	11 Na 23.00	12 Mg 24.32	13 Al 27.1	14 Si 28.3	15 P 31.04	16 S 32.06	17 Cl 35.46
18 Ar 39.88	19 K 39.10	20 Ca 40.07	21 Sc 44.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93
.....	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 69.9	32 Ge 72.5
.....	33 As 74.96	34 Se 79.2	35 Br 79.92	36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Y 88.7
.....	40 Zr 90.6	41 Nb 93.5	42 Mo 96.0	43 —	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7
.....	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 J 126.92
54 X 130.2	55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.6	60 Nd 144.3	61—62 Sm 150.4
63 Eu 152	64 Gd 157.3	65 Tb 159.2	66 Ds 162.5	67 Ho 163.5	68 Er 167.7	69 Tm 168.5	70 Yb 173.5
71 Lu 175.0	72 Hf 178.5	73 Ta 181.5	74 W 184.0	75 —	76 Os 190.9	77 Ir 193.1	78 Pt 195.2
.....	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.20	83 Bi 208.0	84 Po (210.0)	85 —
86 Em (222.0)	87 —	88 Ra 226.0	89 Ac (227)	90 Th 232.15	91 Pa (234)	92 U 238.2	.....

Elements, the atomic numbers of which are not in the order of atomic weights, are in italics. The numbers corresponding to missing elements are in bold-faced type.

1 Hydrogen	24 Chromium	47 Silver	70 Ytterbium
2 Helium	25 Manganese	48 Cadmium	71 Lutecium
3 Lithium	26 Iron	49 Indium	72 Hafnium
4 Beryllium	27 Cobalt	50 Tin	73 <b>Tantalum</b>
5 Boron	28 Nickel	51 Antimony	74 <b>Tungsten</b>
6 Carbon	29 Copper	52 Tellurium	75 —
7 Nitrogen	30 Zinc	53 Iodine	76 Osmium
8 Oxygen	31 Gallium	54 Xenon	77 Iridium
9 Fluorine	32 Germanium	55 Caesium	78 Platinum
10 Neon	33 Arsenic	56 Barium	79 Gold
11 Sodium	34 Selenium	57 Lanthanum	80 Mercury
12 Magnesium	35 Bromine	58 Cerium	81 Thallium
13 Aluminium	36 Krypton	59 Praseodymium	82 Lead
14 Silicon	37 Rubidium	60 Neodymium	83 Bismuth
15 Phosphorus	38 Strontium	61 —	84 Polonium
16 Sulphur	39 Yttrium	62 Samarium	85 —
17 Chlorine	40 Zirconium	63 Europium	86 Emanation
18 Argon	41 Niobium	64 Gadolinium	87 —
19 Potassium	42 Molybdenum	65 Terbium	88 Radium
20 Calcium	43 —	66 Dysprosium	89 Actinium
21 Scandium	44 Ruthenium	67 Holmium	90 Thorium
22 Titanium	45 Rhodium	68 Erbium	91 Uranium X <sub>1</sub>
23 Vanadium	46 Paladium	69 Thulium	92 Uranium



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